An updated overview of diamond-like carbon coating in tribology


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During the last two decades, the industry (including scientists) has focused on diamond-like carbon (DLC) coating because of its wide range of application in various fields. This material has numerous applications in mechanical, electrical, tribological, biomedical, and optical fields. Severe friction and wear in some machine parts consumes high amount of energy, which makes the process energy inefficient. Thus, DLC coating can be an effective means to lower the friction and wear rate. Some important process variables that affect the tribological characteristics of DLC coating are adhesion promoter intermediate layer, substrate surface roughness, hydrogen incorporation or hydrogen non involvement, and coating deposition parameters (e.g., bias voltage, etching, current, precursor gas, time, and substrate temperature). Working condition of DLC-coated parts also affects the tribological characteristics, such as temperature, sliding speed and load, relative humidity, counter surface, and lubrication media (DLC additive interaction). Different types of lubricated oils and additives are used in engine parts to minimize friction and wear. DLC can be coated to the respective engine parts; however, DLC does not behave accordingly after coating because of lubricant oil and additive interaction with DLC. Some additive interacts positively and some behave negatively because of the tribochemical reactions between DLC coating and additives. Numerous conflicting views have been presented by several researchers regarding this coating additive interaction, resulting in unclear determination of true mechanism of such interaction. However, lubricant additive has been established to be more inert to DLC coating compared with uncoated metal surface because the additive is fabricated in such a way that it can react with metal surfaces. In this article, the tribological characteristics of different types of DLC coating in dry and lubricated conditions will be presented, and their behavior will be discussed in relation to working condition and processing parameters.

Keywords  diamond-like carbon, tribology, lubrication, coefficient of friction, wear rate

Table of Contents

1. INTRODUCTION ............................................................................................................................... 1

2. TRIBOLOGICAL CHARACTERISTICS ................................................................................................ 4

   2.1. Types of DLC Coatings and Their Tribological Characteristics .................................................... 4
   2.1.1. Effect of Hydrogen on DLC Coating ............................................................................................. 4
   2.1.2. Effect of sp³/sp² Ratio ...................................................................................................................... 5

   2.2. Deposition Techniques ................................................................................................................... 5

   2.3. Adhesion with the Substrate ......................................................................................................... 6
   2.3.1. Intermediate Layer ......................................................................................................................... 6
   2.3.2. Argon Cleaning .............................................................................................................................. 7
   2.3.3. Surface Roughness ....................................................................................................................... 8

   2.4. Friction ........................................................................................................................................... 8
   2.4.1. Relative Humidity ......................................................................................................................... 8

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Color versions of one or more figures in this article can be found online at www.tandfonline.com/bsms.
2.4.2. Temperature ................................................................................................................................. 8
2.4.3. Doping ............................................................................................................................................... 9
2.4.4. Sliding Speed and Load ................................................................................................................... 11
2.4.5. Counter Face ................................................................................................................................... 13
2.5. Wear .................................................................................................................................................. 13
2.5.1. Relative Humidity ............................................................................................................................ 13
2.5.2. Temperature ..................................................................................................................................... 14
2.5.3. Doping ............................................................................................................................................. 15
2.5.4. Sliding Velocity and Load .................................................................................................................. 16
2.5.5. Counter Face .................................................................................................................................. 17
2.6. Lubrication .......................................................................................................................................... 17
2.6.1. DLC–Extreme Pressure (EP) Additive Interaction ............................................................................ 19
2.6.2. DLC–AW Additive Interaction ........................................................................................................... 21
2.6.3. DLC–FM Additive Interaction ........................................................................................................... 21
2.6.4. DLC–Organic FM Additive Interaction ............................................................................................ 22

3. CONCLUSIONS .................................................................................................................................... 23

FUNDING .................................................................................................................................................. 23

REFERENCES ............................................................................................................................................. 23

1. INTRODUCTION

Diamond-like carbon (DLC) coating is widely used because of its good tribological characteristics and aesthetic value.\(^1\) Tribology consists of three parts, i.e., friction, wear, and lubrication. Coefficient of friction (CoF) and wear are the main parameters in determining the tribological characteristics of DLC coating. DLC can be used as a solid lubricant. Some parts cannot be lubricated by wet lubricants; therefore, DLC can be useful on specific applications, such as food processing, chemical pumps, biological applications, space technology and hard disks.\(^2\)

Different types of DLC coating are available and every type cannot be used as a solid lubricant. Important DLC subclasses comprise hydrogen-free DLC, which is referred to as tetrahedral amorphous carbon (ta-C) and amorphous (a-C), as well as hydrogenated amorphous network of carbon and hydrogen (a-C: H). These subclasses are all grouped as non doped DLC and other classes as doped DLC. Some structural differences are observed among non doped coatings because of the difference in bonding types. In DLC coatings, certain portions of the bonding are sp\(^2\) graphitic bonding and the remaining portions are sp\(^3\) diamond-like bonding. Figure 1 shows the ternary phase diagram of sp\(^2\), sp\(^3\), and hydrogen content in different types of DLC coating. Different types of metal and nonmetal elements can be doped in the DLC matrix to enhance the tribological characteristics. Among these elements are Ti, Si, W, Mo, Fe, Cu, N, F, and Cr, which are frequently being used as dopants.

DLC coating has beneficial effects both in dry and lubricated conditions. DLC coating is known as a dry lubricant. When two surfaces slide against each other, the general rule is that the softer material will wear out. Although DLC exhibits higher hardness compared with the counter mating surface, the wear of DLC is pronounced and forms a film known as transfer layer onto the counter surface. This transfer layer protects the counter surface from wear and lowers the CoF because the transfer layer material is mainly of graphitic structure that has a lubricating effect. Graphite is a layer-by-layer structure. Among the layers, weak van der Waals force exists, so the layers easily slide among one other. As a result, low CoF is observed. Although every type of DLC coating has some positive effects on improving the friction property compared with the uncoated parts, different types of DLC coating have different values of CoF and wear rate. Table 1 shows the database of CoF and wear rate of different DLC coatings in different environmental conditions.

Most modern mechanical systems are operated under high loads, high temperature, and corrosive environment.\(^3\) DLC-coated machine parts can be operated under high load, high temperature (close to 500°C), and under corrosive environment. DLC coating is also becoming commercially attractive because of some of its inherent properties, such as low friction, high wear resistance, and high hardness. In mechanical systems, low friction signifies highly efficient system, which consumes lower energy. Currently, people are very conscious about energy consumption because mineral fuel resources are limited. Thus, several scientists focus on DLC coatings to employ in mechanical systems, which are highly prone to frictional power loss. Therefore, various studies have been performed in different mechanical components, such as...
automotive valve train application, bearings, gears, piston rings, piston pins, direct-injection fuel systems, and cutting and forming tools. These components can be coated with DLC. Table 2 shows different types of coating applied to different engine parts.

Most mechanical systems are used in lubricated condition. Thus, DLC coating behavior under lubricated condition is important. To achieve appropriate property under lubricated oils and additives, some interactions are essential for low friction and wear rate. However, DLC coating is inert to oils and additives compared with uncoated steel surfaces. Some papers show the chemical interaction with DLC coating oil and additives, whereas some reports state absent or negative interaction with DLC (only for non-doped DLC, interaction with MoDTC additive). Thus, contradictions are noted on the interaction with coatings and additives. However, in most cases of metal-doped DLC, researchers have observed some interactions by investigating the tribofilm exposed in oils and additives. Different types of additives behave differently. In most cases, extreme pressure (EP) additives have beneficial effects. In some cases, anti-wear (AW) additives, such as zinc dialkyldithiophosphates (often referred to as ZDDP) additives,

![FIG. 1. Ternary phase diagram for various DLC films with respect to their sp³, sp² type bonding and hydrogen content in the structure. (© Elsevier. Reproduced with permission of Love et al.)](image)

### Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>CVD diamond</th>
<th>Non Hydrogenated DLC</th>
<th>Hydrogenated DLC</th>
<th>Doped DLC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic sp³</td>
<td>sp³</td>
<td>sp² &amp; sp³</td>
<td>sp² &amp; sp³</td>
<td>sp² &amp; sp³</td>
<td>20–39</td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>—</td>
<td>&gt;1%</td>
<td>10–50%</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>μ in vacuum</td>
<td>0.02–1</td>
<td>0.3–0.8</td>
<td>0.007–0.05</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>μ in dry N₂</td>
<td>0.03</td>
<td>0.6–0.7</td>
<td>0.001–0.15</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>μ in dry air</td>
<td>0.08–0.1</td>
<td>0.6</td>
<td>0.025–0.22</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>5–15% RH</td>
<td>—</td>
<td>0.05–0.23</td>
<td>0.02–0.5</td>
<td>0.03–0.4</td>
<td></td>
</tr>
<tr>
<td>μ in humid air</td>
<td>0.05–0.15</td>
<td>0.05–0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15–95%</td>
<td>—</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ in water</td>
<td>0.002–0.08</td>
<td>0.07–0.1</td>
<td>0.01–0.7</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>μ in oil</td>
<td>—</td>
<td>0.03</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>K in vacuum</td>
<td>1–1000</td>
<td>60–400</td>
<td>0.0001</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>K in dry N₂</td>
<td>0.1–0.2</td>
<td>0.1–0.7</td>
<td>0.00001–0.1</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>K in dry air</td>
<td>1–5</td>
<td>0.3</td>
<td>0.01–0.4</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>5–15% RH</td>
<td>—</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K in humid air</td>
<td>0.04–0.06</td>
<td>0.0001–400</td>
<td>0.01–1</td>
<td>0.1–1</td>
<td></td>
</tr>
<tr>
<td>K in water</td>
<td>0.0001–1</td>
<td></td>
<td>0.002–0.2</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>K in oil</td>
<td>—</td>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

μ refers to coefficient of friction
K refers to wear rate [$10^{-6}$mm³(Nm)^{-1}]
Me refers to metal, such as W, Ti, Mo, Fe, V...
X refers to nonmetal, such as Si, O, N, F, B...

![Downloaded by [University of Malaya] at 01:43 26 March 2015](image)
have been proven to function as catalysts in increasing the reactivity of the friction modifier (FM) additive, such as molybdenum dialkyldithiocarbamate (often referred to as MoDTC). This process is achieved by the assistance of AW additives in the formation reaction of MoS2. However, interaction level varies with temperature variation, types of additive present, lubricating base oils, and so on.

DLC coating offers a wide range of properties that can be used in a wide range of applications. Therefore, DLC coating has motivated scientists to conduct further research to obtain new insights in this field for the most efficient application. This article will highlight both processing parameters and environmental conditions that can affect the tribological characteristics of DLC coating both in dry and oil-lubricated condition.

2. TRIBOLOGICAL CHARACTERISTICS

Tribological characteristics strongly depend on the processing technique, use of dopant, and atmospheric conditions during operation. The mechanism and influencing parameters for better tribological property of DLC coating are discussed below.

2.1. Types of DLC Coatings and Their Tribological Characteristics

Most DLC films are structurally amorphous. Depending on the DLC coating structure, as well as hydrogen and other dopant content in the DLC coating, these materials can be classified into several types. DLC is mainly of two types, i.e., hydrogenated and non hydrogenated. Both hydrogenated and non hydrogenated DLC can be doped by some metal and nonmetal dopants. Metals and nonmetals are added based on DLC coating applications. Non hydrogenated DLCs are a-C and ta-C, whereas hydrogenated DLCs are a-C:H and ta-C:H. The ta-C type has higher percentage of sp³ content in the structure (Figure 1). Some metal (e.g., Fe, Ti, Cr, V, Ni, Au, Cu, Nb, W, Mo, Ta) and nonmetal (e.g., Si, N, B, F, O, P) dopants are commonly used.

2.1.1. Effect of Hydrogen on DLC Coating

Hydrogen incorporation in DLC coating has an important function on the tribological characteristics of DLC coating in different environmental conditions. In his article, Erdemir discussed the influence of hydrogen incorporation in DLC, both in inert air- and normal air-exposed environments. The test results suggest that in an inert environment, CoF of non hydrogenated DLC is higher than that of hydrogenated DLC.

<table>
<thead>
<tr>
<th>Engine component</th>
<th>Substrate</th>
<th>Coating</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve</td>
<td>X20CrMo V121 steel</td>
<td>chromium carbide</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>M2 tool steel</td>
<td>DLC</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>chromium</td>
<td>42</td>
</tr>
<tr>
<td>bearings</td>
<td>AISI 52100 steel</td>
<td>DLC</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>100Cr6 ball bearings</td>
<td>(Cr,A1)N</td>
<td>43-44</td>
</tr>
<tr>
<td></td>
<td>Cr2N</td>
<td>Cr + nC(nano sized carbon)</td>
<td>45</td>
</tr>
<tr>
<td>Gears</td>
<td>SCM420 alloy</td>
<td>Molybdenum disulphide/titanium (MoS2/Ti)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>DIN 17210 20MnCr5 steel</td>
<td>W-DLC, DLC</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>M42 steel</td>
<td>Carbon/Chromium (C/Cr) composite</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>16MnCr5 and SAE410 steel</td>
<td>thermal sprayed molybdenum</td>
<td>47</td>
</tr>
<tr>
<td>Piston ring</td>
<td>cast iron</td>
<td>Chromium ceramic</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>chromium nitride</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>AISI 440C steel</td>
<td>Al-Mo–Ni</td>
<td>50-51</td>
</tr>
<tr>
<td>Piston pin</td>
<td>Aluminum Alloy 390</td>
<td>DLC</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>52100 steel</td>
<td>CrN</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Phosphatized coating</td>
<td>WC/C coating</td>
<td>54</td>
</tr>
<tr>
<td>Direct injection fuel systems</td>
<td>Ceramic or steel</td>
<td>Ceramic coating</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>AISI 52100 (UNS# G52986) steel</td>
<td>DLC near-frictionless carbon (NFC)</td>
<td>56</td>
</tr>
</tbody>
</table>
Without, when similar coatings are exposed to normal air-
exposed environment, significant decrement of CoF of non
hydrogenated DLC is found, whereas that of hydrogenated
DLC coating increases. Environmental species, such as water
molecules and oxygen, can significantly influence the fric-
tional properties of DLC coatings. Friction in DLC interfaces
may result from covalent bond interaction, van der Waals
forces, electrostatic attractions, and capillary forces between
surfaces in contact. In a dry environment, capillary forces do
not have a significant function in hindering motion; however,
other forces are active, such as covalent bond, $\pi-\pi^*$ interac-
tions and van der Waals forces. The $\pi-\pi^*$ interactions are
active between graphitic carbons, such as sp²-bonded carbon
atoms of DLC films.

Some unbound $\sigma$ bonds are present in the DLC contacting
surface. The elimination of this bond type is important in mini-
mizing the friction force. For hydrogenated DLC, continuous
passivation of this bond is possible using hydrogen, which is
present in the matrix both in atomic and molecular state. This
hydrogen acts as a reservoir. These molecules can continu-
ously passivate those bonds, resulting in lower surface energy.
This process effectively minimizes friction.

Intense hydrogen bombardment during hydrogenated DLC
deposition prevents the formation of cross-linking or C=C
double bonding in DLC film. Therefore, $\pi-\pi^*$ interactions
that can result from graphitic carbon can be minimized in hydrogenated DLC contacts in inert environment.

Sometimes two hydrogen atoms are attached to one carbon
atom, which is called di-hydrated carbon atom. These di-
hydrated carbon atoms on DLC surface provide better shield-
ing by providing higher degree of passivation. Therefore,
elimination of strong covalent $\sigma$ bond and $\pi-\pi^*$ interaction, as
well as the possibility of obtaining di-hydrated carbon in the
DLC are the major reasons for the superlubricity of hydrogen-
ated DLC. In an air-exposed environment, increments of fric-
tion caused by capillary forces are noted around the real
contact area. Capillary force increases because water mole-
cules are adsorb in the surface.

By contrast, non hydrogenated DLC has a higher chance of
obtaining dangling carbon bond in the surface. In an air-
exposed environment, these free dangling carbon bonds can be
passivated by absorbed water molecules, oxygen, and hydro-
gen from the surrounding environment. When such surfaces
are exposed to an inert environment, such contact cannot be
passivated by environmental species. Therefore, fresh $\sigma$
 bonds and $\pi-\pi^*$ interactions are enhanced, which results in higher
friction in inert or vacuum environment.

2.1.2. Effect of sp³/sp² Ratio

The sp³/sp² ratio is an important factor that determines the
tribological characteristics of different types of DLC coating.
ta-C has the highest percentage of sp³ content (80% to 88%) in
its structure. In addition, sputtered carbon, which often
referred to as amorphous carbon (a-C), contains lowest amount
of sp³ content (5%) in its structure. Both of these compounds
are non hydrogenated DLC. The hydrogenated tetrahedral
DLC (ta-C:H) and amorphous hydrogenated (a-C:H) hard
DLC contains about 70% and 40% sp³ content in their struc-
ture, respectively. Robertson58 mentioned in his article that a-
C:H DLC has two subclasses: one subclass is hard, and the
other is soft. The basic difference between the two subclasses
is noted on their hydrogen content in their structure. That is,
hard coating has lower hydrogen percentage (30–40%) and
soft coating, which is basically known as polymeric a-C:H
coating, is composed of 40–50% hydrogen. The hardness of ta-C, ta-C:H, and a-C:H hard coatings vary according to their
sp³ content in the structure. Higher sp³ content percentage
shows higher hardness value. Although soft a-C:H DLC has
higher percentage of sp³ content in its structure, this materials
has decreased hardness. Sputtered carbon a-C coating has 5%
sp³ content and 15 GPa hardness.59

Ronkainen et al.29 investigated the tribological characteris-
tics of ta-C and a-C:H DLC in dry environment. Although a-
C:H and ta-C DLC have high proportion of sp³ bonding in the
structure, the transformation to graphitic structure is more pro-
nounced for a-C:H DLC. Due to friction-induced heating,
some hydrogen depleted regions are formed. These regions are
the hot spots for graphitization because C–H bonds can easily
break down in friction-induced heating. However, ta-C con-
taining sp³ bonding is more stable than the sp³ bonding of a-C:
H; therefore, graphitization rate is low in ta-C DLC. In addi-
tion, transfer layer formation is less pronounced for ta-C DLC
compared to a-C:H DLC, and ta-C DLC is a very hard
(80 GPa) coating; therefore, counter surface wear rate is high.
Another factor might affect the a-C:H/ta-C:H contact friction
(i.e., electrostatic repulsive force), which facilitates the slip of
each layer over the other, because a repulsive force exists
among the C–H bonds of the contact pair.57

2.2. Deposition Techniques

Deposition technique is one of the important factors that
influence DLC coating property. Currently, several kinds of
deposition methods are in depositing DLC films. A wide range
of deposition temperature is observed for DLC coating. This
temperature may vary from sub-zero to 400°C. Deposition gas
pressure, bias voltage, and etching time can also be varied
over broad ranges depending on the type of deposition method
being used. Researchers are interested on DLC coating
because of its high degree of flexibility. Some of the types of
deposition techniques are ion beam deposition, magnetron
sputtering, plasma immersion ion implantation and deposition
(PIII-D), and plasma-activated chemical vapor deposition
(PACVD). These techniques are discussed briefly.

In the ion beam deposition technique, a combination of lin-
cear ion gun with hydrocarbon gas, an inert gas, and a sputter
gun for interlayer deposition is used. In the ion gun, a collision
is noted between electrons; this collision is confined in the magnetic field with gas molecules, and as a result, gas molecules are ionized. In the discharge area, the anode (positively biased) repels the ion and accelerates these molecules away from the source. This process subsequently creates an ion beam. At a fixed anode voltage, the ion beam gets deposited on the negatively biased substrate material. An atomic collision is observed between the incoming ions and substrate atoms; thus, the atomic mobility and chemical reactivity are athermally enhanced. Therefore, the processing temperature for epitaxial growth and metastable compound formation in the subsurface region is quite low.60 Plasma density and discharge current will increase with the increment of applied gas pressure and voltage.61 The above-mentioned processes state the gist of ion beam deposition technique.

At present, magnetron sputtering is a widely used process for DLC coating. This technique can be employed to DLC coating for both hydrogenated and non-hydrogenated conditions. Puchi-Cabrera et al.62 used this technique for hydrogenated DLC coating (a-C:H) deposition. They deposited a Cr interlayer to promote DLC coating adhesion. Butane gas was used as a carbon and hydrogen source. Peng et al.63 coated non-hydrogenated DLC through the same process; however, they used pure graphite source for deposition. Non-hydrogenated films up to 1 μm thick were prepared by sputtering from a pure graphite target in Ar plasma. The basic mechanism for magnetron sputtering is described as follows: a target plate (cathode) is bombarded by energetic ions generated from glow discharge plasma, which is situated in front of the target. Through the bombardment process, the removal of target atoms take place and these atoms condense on the substrate as a thin film. Secondary electrons are also emitted from the target surface as a result of ion bombardment, and these secondary electrons help in maintaining the plasma. Magnets are placed in a manner that is parallel to the target, which results in the trapping of secondary electron; thus, the probability of atom electron collision increases, which helps in sustaining the plasma.64,65

PIII-D is a known technique because this technique is used in producing DLC coating on large parts and complicated shape at room temperature. Therefore, this technique is potentially useful in coating medical device with irregular geometry.66 Kwok et al.67 used this technique for Ca- and P-doped DLC coating. They used two containers; and each of these containers contains pure Ca and P, which was heated with heating filament for evaporation. A negative bias voltage was imposed while the substrate was in positive bias voltage. They used C2H2 gas as a carbon and hydrogen source, and used Ar to create plasma. In this technique, when appropriate pressure and pulsed bias voltage are applied, breakdown of molecules will take place and plasma will be generated. Generated plasma can sustain for a few milliseconds after the pulse is turned off. Thus, if the pulse repetition frequency is large enough, then glow discharge can be formed in the next pulse without former breakdown. In this process, an ion sheath will be formed between the plasma and the inner surface. Consequently, the ions in the sheath will be accelerated by the potential difference of the ion sheath; thus, bombardment will take place and DLC structure will be generated through this method.68

PACVD is a good technique for DLC coating deposition. Plasma can be maintained by different techniques, such as direct current, radio frequency, and direct current bipolar pulse.69 Towe et al.70 deposited Ti and Fe containing DLC by PACVD process. They used various solid volatile precursor materials, such as ferrocene [Fe(C5H5)2], cyclooctatetraeniron-tricarbonyl [C8H8Fe(CO)3], methyl-cyclopentadienyl-iron-dicarbonyl [CpFeCH3(CO)2], and fluid titanium ethoxide for the deposition of DLC coating doped with Fe and Ti. PACVD technique combines some of the benefits of both PVD and CVD process. In this technique, the process temperature is low and can be used for coating on steel substrate.71 In addition, the substrate is located outside the plasma glow region. The gas that is entering from outside into the deposition chamber flows through the discharge volume. In the discharge volume, reactive species are produced that collide with the substrate and produce a film.72,73 Background pressure lower than 2×10⁻³ Pa is maintained by a diffusion pump and the operating pressure. Such pressure is controlled by admitting valves, which ranges from 0.1–1 Pa. Figure 2 shows the schematic diagram of different processes described above.

2.3. Adhesion with the Substrate

DLC coating can show the desired property if the adhesion between the substrate and coating materials is strong enough. On every substrate, DLC coating cannot be directly applied because the materials cannot deposit strongly onto the substrate. Thus, the substrate needs assistance from a third party, which is an adhesion promoter intermediate layer. DLC can be deposited above the adhesion promoter intermediate layer. Therefore, the interlayer should be selected as if such layer can stick to the substrate and coating strongly. Silicon and chromium are used as an intermediate layer in most cases. Some variables affect adhesion onto the substrate, which are briefly discussed below.

2.3.1. Intermediate Layer

Intermediate layer should be selected according to the substrate. Jun et al.76 used Si interlayer to coat DLC on tool steel substrate. Jones et al.77 used TiC–TiN interlayer for Ti substrate. Some researchers coat stainless steel substrate using Cr interlayer. If the interlayer is not used, then the coating can delaminate when exposed at low load. The thickness of the interlayer should be thin enough because as the thickness increases, a decrement of residual stress is noted and the probability of inside crack formation of the intermediate layer will be increased considerably.76 As the compressive stress of the interlayer increased, the total residual stress of the coating is
found to increase as well. This change results in higher shear force at the interface, which subsequently led to higher deposition of adhesive coating.\textsuperscript{78}

2.3.2. Argon Cleaning

Ar cleaning is an important factor that can promote coating adhesion. Jun et al.\textsuperscript{76} showed how Ar cleaning works in promoting adhesion property. They investigated the scratch track with respect to Ar cleaning time, and found that with the increment of Ar cleaning time adhesion property also increases. However, excessive time can damage the surface; therefore, time is optimized better. Another factor is the negative bias voltage of Ar cleaning, i.e., at higher negative bias voltage, better adhesion occurs. Morshed et al.\textsuperscript{79} showed that as the etching time varies, a slight change is observed in the

![Schematic diagram of different deposition techniques](image-url)
Surface composition of the element. This change affects adhesion. They showed their result through Fourier transform infrared spectroscopy (FTIR).

2.3.3. Surface Roughness

Surface roughness has a strong effect on the adhesion property of DLC coating onto the substrate. Rougher surface shows better adhesion with the substrate. Ohana et al. showed that smooth surface that has a surface roughness (Ra) of 1.4 nm leads to severe damage at a load of 9.4 N, which was deposited by pulsed bias CVD method. However, the film that was deposited on a substrate that has a roughness Ra = 263 nm showed no damage at the same load. Some discrepancies may be noted for different deposition processes on coating adhesion with the substrate and effect of surface roughness on friction and wear behavior.

Rougher surface shows better adhesion, but wear rate of counter surface increases severely. Jiang and Arnell showed the effect of substrate surface roughness on the wear rate of DLC coating in dry condition. They found that after certain roughness (Ra = 0.93), the wear rate of the coating increased rapidly. Therefore, optimum value should be considered.

2.4 Friction

DLC coating is used as a solid lubricant to minimize the friction between two surfaces. The mechanism by which DLC coating functions in reducing the CoF depends on many factors, such as relative humidity, counter face, normal load, sliding speed, doping, and temperature.

2.4.1. Relative Humidity

Tribological behavior of DLC coating is highly sensitive to some environmental factors, especially on relative humidity. In general, CoF decreases with decreasing relative humidity of hydrogenated DLC coating (a-C:H). Kokaku et al. reported that when a film is exposed to relative humidity of 90%, surface layer oxidation takes place. Yoon et al. discussed the chemical change that occurs during humidity change. They suggested that a friction layer forms by the reaction between oxidized DLC films with ferrous oxide. Due to humidity, formation of carboxylic acid is pronounced and may result in the formation of friction layer.

Huu et al. reported that hydrogen is weakly bonded in vacuum condition and strongly bonded in moist condition. In addition, the repulsive force in the surface acting on C–H bond decreases to a value of 80 times in moist condition with respect to the vacuum condition. In vacuum, hydrogen desorption takes place. This process lubricates the counter surfaces in contact. Thus, the CoF for hydrogenated DLC (a-C:H, ta-C: H) is decreased. According to Maruyama et al., when hydrogen in the surface interacts with the absorbed water layer oxygen, an increase in CoF occurs. Therefore, a small amount of water vapor inhibits the lubricating property of hydrogenated DLC.

An opposite trend can be found when the relative humidity dependency between the non hydrogenated (a-C) and hydrogenated (a-C:H) DLC is compared. When the CoF is decreased, an opposite trend is observed with increased humidity in the case of (a:C) DLC. In the case of (a-C:H) DLC, CoF initially increases up to a certain humidity level and then decreases. Highest CoF at a specific humidity is called critical humidity. The reason behind the low CoF of the (a-C:H) DLC in low humidity region lies in the friction mechanism. During the sliding process by frictional heating, a graphitization process occurs and the graphite layer forms in the counter surface, which results in easier sliding between layers. By increasing humidity, the graphitization process actually decelerates and the CoF increases. In the case of (a-C) DLC coating, humidity works as a lubricant. If there is no hydrogen to react, then the adhesive force between the sliding surfaces hinders the motion during sliding.

The van der Waals forces, π–π interactions, capillary forces, and electrostatic attraction may be present between sliding surfaces to increase the adhesion. The severity of π–π interaction can be minimized by the presence of water in the test environment. In the case of ta-C films, CoF decreases with increasing humidity because water molecule intercalates between the graphite layers; and therefore facilitate their slip over each other. Figure 3 shows the friction interaction of DLC coating in different environmental condition.

2.4.2. Temperature

Temperature greatly affects frictional property. As the temperature increases, a trend to increase the coefficient of friction is observed. Graham et al. coated W-doped DLC coating on silicon substrate. They tried to determine the elevated temperature effect on the CoF and wear property, and obtained the result according to Figure 4. As the temperature increases above 250°C, transformation from sp^3 to sp^2 graphite-like bond occurs. Graphite functions as a solid lubricant because this material has a layer-by-layer structure. Van der Waals bond are noted between each layer. This bond is very weak; therefore, each layer can slide relative to the other layer easily. That is the reason why a decrement of CoF is noted. In lower temperature region, as the temperature increases, the gradual increment of CoF is for moisture depletion caused by the evaporation process of the water molecule, which is attached to the coated surface. Wang et al. showed the oxidation behavior of DLC coating by thermo gravimetric analysis (TGA). They found that in the temperature range from 350–400°C, severe oxidation occurs and affect the frictional property. Some differences in the frictional properties were observed in case of hydrogenated DLC and non hydrogenated DLC. Gao et al. showed that heating of a-C:H DLC structures to 147°C caused significant amount of hydrogen desorption from the a-C:H
coating surface. As a result, CoF also increases. In general, at elevated temperature, wear rate increases and CoF decreases. Through doping process, graphitization temperature can be changed to higher temperature, especially through silicon doping.97

Phase transformation and oxidation temperature for non hydrogenated DLC is much higher than that for hydrogenated DLC. If ta-C film is annealed in vacuum, then the structure will be stable up to 727°C. If heated in air, film oxidation is observed from 450–500°C.58 Therefore, the CoF of non hydrogenated DLC will be stable at higher temperature compared to hydrogenated DLC. Behavior of non hydrogenated amorphous carbon a-C is different from ta-C. DLC (a-C) film deposited by magnetron sputtering are reported to be thermally stable up to 300°C. Beyond 300°C, the hardness value drastically drops because of graphitization of the coating structure. CoF increases at elevated temperature testing. The increased friction coefficient is due to the absence of water in the tribocontact.98

2.4.3. Doping
Carbon-based coating shows high residual stress, poor adhesion to the substrate, and low toughness. So far, two types of methods have been performed to solve such problems:

1. the use of soft intermediate layer to absorb or release stress, or the use of hard transition layer to improve the adhesion, and
2. the incorporation of transition metal atoms into the carbon atom network.

Some metals and non metals can be added as a dopant to enhance some coating properties mentioned in earlier section (Section 2.1). Their effects will be discussed briefly in the following sections.

2.4.3.1. Silicon Containing DLC. Ikeyama et al.99 investigated the property of DLC coating doped with Si. Si doping releases internal stress, which results in decreased hardness. Si
doping increases the Si–C (four-fold co-ordinated network) bridging bond and can also weaken the adjacent C–C bond, which causes decreased hardness.\textsuperscript{100,101} By doping with Si, the sp\textsuperscript{3}/sp\textsuperscript{2} ratio increases because silicon does not form π bonds.\textsuperscript{101,102} Some contradictory literatures suggests that by doping with silicon, hardness and sp\textsuperscript{3}/sp\textsuperscript{2} ratio increases.\textsuperscript{103} Varma et al.\textsuperscript{103} deposited Si–DLC films on Si wafers using energetic Ar\textsuperscript{+} ion assisted beam bombardment of a vapor-deposited precursor material, i.e., tetraphenyl-tetramethyl-trisiloxane. They have deposited Si–DLC at different deposition parameters, and they found highest hardness on the films that possess the highest amount of sp\textsuperscript{3}/sp\textsuperscript{2} bonding ratio and on the films deposited in low current density. They suggested that Si is participating in the DLC structure by tetrahedral bonding with hydrogen and CH\textsubscript{n}. Si incorporation in DLC structure seems to suppress aromatic ring structure formation. Low current density during the deposition favors the Si incorporation in tetrahedral Si–C, which is more diamond like. Therefore, diamond-like behavior is enhanced, which results in increased hardness. Table 3 provides the literature survey results of the relationship of doping element in DLC to sp\textsuperscript{3}/sp\textsuperscript{2} ratio and hardness change due to doping.

Oguri et al.\textsuperscript{40,104} deposited a-C:H:Si DLC by d.c. PACVD technique and tested the samples at 60% relative humidity; they found that the CoF ranges between 0.03 and 0.1. During the tribology test of the samples, SiO\textsubscript{2} particles are formed, which further interacts with Si(OH)\textsubscript{4} formed under environmental humidity. Si(OH)\textsubscript{4} is a gel-like substance; therefore, this compound promotes sliding during friction.\textsuperscript{105,106}

An increase in internal stress is associated with an increase in silicon content. Unlike metal-containing films, the a-C:H:Si films are amorphous and exhibited friction coefficient lower than 0.1. Donnet\textsuperscript{26} mentioned in his review paper that Meneve et al. investigated the tribological behavior of a-Si:C:H films deposited by PACVD process. They found that addition of silicon to a-C:H film reduces the hardness, elastic modulus, and internal stresses by 15–30%. In humid conditions, potential applications of these films are limited to contact pressure levels below approximately 1 GPa.

Donnet\textsuperscript{26} summarizes the effect of Si incorporation in the DLC structure on tribological behavior. Friction appears to be significantly reduced compared to conventional undoped DLC in ambient humid air in low load application (>1 GPa). At higher contact pressures, conventional a-C and a-C:H films cannot be surpassed. a-C:H:Si can be used in moderate mechanical conditions, for low-stress aerospace or automotive component protection, precision ball bearings and gears, sliding bearings, and magnetic recording media.

### 2.4.3.2. Fluorine-containing DLC

By doping with F in the a-C:H DLC, surface energy can be reduced to 20 mN m\textsuperscript{−1}, and the surface energy of undoped a-C:H DLC is 43 mN m\textsuperscript{−1}. However, hardness becomes slightly lower than undoped a-C:H. Si and F both are unable to form double bond with carbon;

<table>
<thead>
<tr>
<th>Coating</th>
<th>Substrate</th>
<th>Intermediate layer</th>
<th>Deposition process</th>
<th>Changes in sp\textsuperscript{3}/sp\textsuperscript{2} ratio compared to nondoped DLC</th>
<th>Hardness changes due to doping compared to nondoped DLC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-DLC</td>
<td>Si wafer</td>
<td>—</td>
<td>Ion beam-assisted deposition (tetraphenyl-tetramethyl-trisiloxane precursor material)</td>
<td>increases</td>
<td>increases</td>
<td>103</td>
</tr>
<tr>
<td>a-C:H:Si</td>
<td>Mirror polished stainless steel</td>
<td>—</td>
<td>Bipolar pulsed PBII</td>
<td>increases</td>
<td>decreases</td>
<td>142</td>
</tr>
<tr>
<td>a-C:H:Si</td>
<td>Acrylonitrile Butadiene Rubber</td>
<td>—</td>
<td>Unbalanced magnetron sputtering ion platting</td>
<td>increases</td>
<td>decreases</td>
<td>134</td>
</tr>
<tr>
<td>a-C:H:Si</td>
<td>Acrylonitrile Butadiene Rubber</td>
<td>Si-C</td>
<td>Unbalanced magnetron sputtering ion platting</td>
<td>increases</td>
<td>decreases</td>
<td>134</td>
</tr>
<tr>
<td>a-C:Ti</td>
<td>Stainless steel 316L</td>
<td>—</td>
<td>Closed field unbalanced magnetron sputtering</td>
<td>increases</td>
<td>increases</td>
<td>138</td>
</tr>
<tr>
<td>Ti-DLC</td>
<td>polished Si and stainless steel</td>
<td>Ti</td>
<td>DC-PECVD</td>
<td>decreases</td>
<td>decreases</td>
<td>143</td>
</tr>
<tr>
<td>a-C:H:W</td>
<td>AISI 52100 steel balls and discs</td>
<td>—</td>
<td>PVD/PECVD</td>
<td>decreases</td>
<td>decreases</td>
<td>144</td>
</tr>
</tbody>
</table>

**TABLE 3**

Different doped DLC coating changes in structure and effect in hardness
lowers the surface energy. Variation in C–CF, CF, and CF2 decreases, and reduced dispersive component in the surface of F incorporation in DLC enhances sp2 hybridization. Pressure and the F transfer will lead to the formation of a stable AlF3 compound at the Al surface. The generation of repulsive forces between two F-passivated surfaces, as a result of the F transfer to the Al surface, was shown to be responsible for the low CoF between Al and F–DLC.

In summary, very high F percentage is not desirable in DLC film. Although very high F percentage reduces the surface energy, hardness value is decreased. sp2 hybridization is enhanced, which deviate the coating from diamond-like properties. In tribological application, more sp2 type bonding is desirable. Researchers are interested in biomedical application because of hydrophobicity and biocompatibility of fluorinated DLC.

2.4.3.3. Nitrogen-containing DLC. Mainly four types of N-doped DLC are synthesized by different deposition techniques. These compounds are a-C:N, ta-C:N, a-C:H:N, and ta-C:H:N. a-C:N can be deposited by reactive magnetron sputtering process. This film can be deposited above 200°C. In addition, this film is nanostructured, and a strong cross-linking is observed between the graphite planes, which increases film hardness. This change does not increase the sp3 fraction, but increases disorder in the film. This effect makes the film used effectively in magnetic storage device. Cutiongo et al. deposited a-C:N film on magnetic disks by sputtering in Ar/N plasma. This film exhibited three to four times better pin-on-disk contact durability compared to the a-C DLC film. Khurshudow et al. deposited a-C:N DLC by ion-beam-assisted deposition technique. This film exhibited low coefficient of friction against silicon nitride ball. Koskinen et al. deposited a-C:N films by the pulsed vacuum arc method on silicon and metal substrates. CoF was measured using pin-on-disk apparatus at various humidity levels. These compounds have steady state CoF between 0.2 and 0.3 at different humidity levels. Friction coefficient was found to increase with increasing N, especially at lower humidity level.

ta-C:N film can be deposited by magnetron sputtering ion beam deposition, pulsed laser deposition (PLD), and filtered cathodic vacuum arc (FCVA). The deposition processes are performed either under N2 atmosphere or N2-assisted beam. Experimental result has been found that up to 10% N content in the tetrahedral carbon film does not change the relative percentage of sp3 content (80–90%) in the film. Beyond 10% N content in the film may cause rapid fall of the sp3 content and film density. High deposition pressure may cause the rapid fall of sp3 content and film density.

a-C:H:N can be deposited by PECVD. Methane, acetylene, and benzene gas are used as a C source, and N2 or NH3 as the N source. High substrate temperature and high N2 content in the gas mixture hinder the N incorporation in the film. Compared to a-C:N, the hardness in the a-C:H:N film decreases with nitrogen content. NH3 and nitrile groups are formed, which are often referred as terminating groups. Higher substrate temperature and bias voltage is not desired, because these parameters favor the graphite-like film formation. Dekempeneer et al. deposited a-C:H:N films using r.f. PACVD process that has a N content between 0 at% to 35 at% depending on the deposition condition used. The N incorporation leads to softer film, and a steady state friction in the ambient air condition remains at 0.2.

ta-C:H:N type DLC films are prepared by a high-density plasma source, such as ECR, or helicon source. Addition of N in the ta-C:H DLC causes sp3 phase clustering up to a certain level of N content (~20%). Moreover, further increment may cause lowering of the sp3 fraction in the DLC film, which results in decreased film hardness.

Very little research has been conducted on the tribological characteristics of N-doped DLC. Some studies have been performed to reveal the tribological characteristics of a-C:N- and a-C:H:N-type N-doped DLC. Therefore, a good research
opportunity is found to reveal the tribological characteristics of ta-C:N- and ta-C:H:N-type DLC.

2.4.3.4. Metal-containing DLC. Metal-doped DLC has been substantially studied because of their improvement in toughness, thermal stability, and tribological characteristics, as well as their relatively lower residual stresses than that of pure DLC films.\textsuperscript{134–137}

Wang et al.\textsuperscript{138} doped with Ti, and found that this element improves adhesion to the substrate, releases internal stress, and increases hardness. In general, if the internal stress is relieved, then DLC film should lose hardness; however, in the current study, the hardness also increases. In this case, Ti reacts with carbon in the matrix and forms carbide. This carbide is very hard; thus, hardness is apparently increased. Ti exists in the Ti-DLC as a displacement of C from C–C bond or solid solution, which deformed the carbon network in the DLC coating structure.\textsuperscript{139} The Ti-C bond formation restricted grain boundary sliding by limiting the intergrain space, increased hardness and load capacity, and had positive effect on friction coefficient reduction.

Lubwama et al.\textsuperscript{140} investigated the frictional property change at different doping conditions and at different sliding conditions. Some other doping agents can be added, such as W and Fe. Chang et al.\textsuperscript{141} tested three types of metal-containing DLC coating (i.e., Cr-C:H, Ti-C:H, and Zr-C:H) and found that Cr-doped DLC provides better frictional property than others in the initial stage, as well as in the steady state condition. Chromium-containing DLC have lower surface roughness; therefore, initial friction coefficient is low. In a steady-state condition, low CoF was maintained because of denser coating compared to other metal-doped DLC.

2.4.4. Sliding Speed and Load

Kim et al.\textsuperscript{145} showed the change in CoF at different velocities and normal load. They found the results according to Figure 5. Figure 5A shows the change of CoF at various loads with increasing velocity. Figure 5B shows the change of CoF at various velocities up to 20 km sliding distance. Figure 5A shows that as the velocity and normal load increases, the CoF decreases. During the sliding period up to 20 km sliding distance at different velocities, friction profile change has been observed and is shown in Figure 5B. This finding confirms the lower CoF at higher velocities. The CoF change depends on the graphitization process. The graphitization temperature of hydrogenated DLC coating is within the range of 400–500°C; and this finding is accompanied by the desorption of hydrogen incorporated in the DLC matrix.\textsuperscript{146} Hydrogen desorption temperature corresponds to the sp$^3$ to sp$^2$ transition temperature. Temperature rise depends on sliding conditions, such as sliding speed and load. Temperature increase also affects the graphitization, and can be measured by the following equations:

\[
\Delta T = \frac{Pv}{1/a(K1 + K2)a},
\]

where $\Delta T$ is the induced temperature rise, $\mu$ is the CoF, $P$ is the applied normal load, $v$ is the sliding speed, $K_1$ and $K_2$ are the thermal conductivities of the coating and the ball, respectively, $a$ is the contact radius of the real contact area, and $H$ is the measured coating hardness. According to Eq. (1), with the increase of sliding speed $v$ and load $P$, contact surface temperature increases; therefore, graphitization enhances. Graphitization results in the lowering of CoF. Increasing the load lowers the graphitization temperature by increasing the contact stress. Further graphitization can be promoted by friction-induced annealing on the local contact areas and sliding-induced strain energy.\textsuperscript{146,148}

![FIG. 5. (A) Friction coefficient change with different velocity at a normal load of 20.7N. (B) Friction coefficient change at different load with the change of velocity. (© Elsevier. Reproduced with permission of Kim and Kim.\textsuperscript{145} Permission to reuse must be obtained from the rightsholder.)](image-url)
2.4.5. Counter Face

Material of the counter face in contact with the DLC coating is an important factor that affects the tribological property. Jia et al. investigated the value of CoF by changing the counter face material at different humidity levels. The change of CoF at different numbers of passes is shown in Figure 6. Figure 6 clearly shows that static CoF is higher for dry condition; however, with increased number of passes, CoF becomes lower irrespective to the specified pairs of sliding interfaces. One possible reason for this finding is that in humid condition, the water layer functions as lubricant and lowers the friction between the pairs. As the number of passes increases, friction tends to be higher compared to a dry condition. The reason behind this finding is that with time, the hydrogenated DLC coating reacts with the oxygen present in the water molecule. Therefore, this process increases the polarity and hinders the motion relative to each other as described in Section 2.3.1. According to Figure 6, in the boundary lubrication condition, the molecule can react with the metal surface; therefore, the other pairs (such as DLC-Si nitride and DLC-steel) show lower CoF compared to the DLC–DLC sliding pair. However, DLC is comparatively inert to the commercially available lubricants; thus, the lubricants cannot function properly, which results in an increased friction.

Ronkainen et al. showed the effect of counter face at different sliding velocity and normal load to the CoF. They used steel and aluminum counterpart and found in both cases CoF decreased with the increment of sliding velocity and normal load. In the case of aluminum counter face, the increase of sliding velocity results in less pronounced trend of decreasing CoF for a-C:H coating (Figure 7). Friction property varies with the type of counter face, material hardness of counter face, and roughness of surface.

2.5. Wear

DLC coating is also used to minimize wear. The same factors (such as friction) also influence the wear mechanism of the sliding interfaces. In some cases, the increasing or decreasing order is different. These factors are described below.

2.5.1. Relative Humidity

Water has a specific effect on the formation of a DLC transferred layer on the counter face. The formation of transferred layer is influenced by H2O and O2. In dry air, the worn counter face is covered by a thick and compact, transferred, carbon-rich layer that helps in preventing the direct contact between the counter face and the DLC film. Water vapor can be condensed on the contact zone with the increment of relative humidity. This process prevents the formation of transferred layer and direct contact between the pairs, which results in the increase of wear. Another reason for this finding is that the dry lubricating effect of DLC is inhibited in this case. In some cases, opposite behavior is observed, which depends on many factors, such as doping condition and counter face. According to Czyzniewski, the humidity level increment causes the decrement of wear rate of the steel counter face and the coating when DLC (a-C:H) is doped with different percentages of W dopant. However, silicon that is doped to the DLC coating in humid condition can increase the wear rate, but decrease the CoF. In the case of DLC (a-C) coating, increased humidity level results in decreased wear rate. This finding is also supported by Jiang et al. According to Rabinowicz, analysis during sliding, the formation of wear debris particles is due to plastic deformation. Rabinowicz also proposed a relationship of the particle size D as a function of material properties and surface energy, γ:

\[ D = K \gamma^\nu P \]  

where K is a material-related constant and P is the yield stress of the wear material. According to Eq. (3), surface energy reduction leads to a smaller particle size of wear debris. These smaller particles of the wear debris are prone to agglomeration. In addition, such particles are compacted to the wear surfaces and form a wear-protective layer. A high relative humidity also assists in further agglomeration and compaction of the wear debris particles to the wear surfaces by the capillary effect. This process further reduces the wear. For the DLC coating that is non hydrogenated was investigated to have a structure that is primarily composed of an amorphous or nano-crystallized framework of sp2 bonding with a smaller fraction of sp3 bonding. The non hydrogenated DLC coatings have a cluster of sp2 bonding with localized ordering. Such cluster on the metallic surface has a cleavage face and edge faces. The cleavage face has a sp2 crystal structure similar to that of graphite. The cleavage face is

![Figure 6. Friction coefficient vs. number of passes at dry and humid condition between different pair of surfaces at a load of 9.8 and velocity 1.6 cm/s. () Cambridge University Press. Reproduced with permission of Jia et al. Permission to reuse must be obtained from the rightsholder.)](image-url)
formed by the basal plane and has a low surface energy. The dangling covalent bond in the edge faces has a high surface energy; thus, such faces can be readily passivated by the moisture or by the other gases from the environment. When the test is performed in a vacuum or dry environment, the newly created surface of the coating caused by the wear of the coated surface cannot be passivated further. Therefore, high adhesion occurs between the surfaces, which results in increased CoF and wear rate. For the hydrogenated DLC coating, a continuous passivation occurs from the inner crystal structure by hydrogen atoms and minimizes the surface energy. As a result, CoF and wear rate do not increase. The high surface energy indicates the large wear debris particles according to Eq. (3), which are easily removed from the rubbing surface; thus, increases the wear loss. Therefore, high wear rate is observed in a dry or vacuum condition for non hydrogenated DLC coating.

2.5.2. Temperature

Working temperature greatly influences the wear rate of the DLC coating and counterface. As shown in the Fig. 4, as the temperature increases from room temperature to 100°C, wear rate increases from $0.5 \times 10^{-5}$ mm$^3$/Nm to $8.5 \times 10^{-5}$ mm$^3$/Nm; then gradually decreases to 400°C; and finally, drops rapidly. Graham et al. coated W-DLC on steel substrate and found the results shown in Figure 4. Relatively low wear rate in room temperature is due to the formation of transfer layer on the aluminum counterface. This layer is found to be lubricious because of atmospheric moisture. The moisture dissociates to H and OH radical and passivates the dangling bond on the surface. This process minimizes the C–C interaction between the sliding interface and the layers. At 25–100°C, a rapid increase of wear rate caused by the depletion of moisture is observed. Such increase is explained by the finding that in this temperature, the moisture evaporates; thus, no passivation occurs. Adhesion between Al–C interfaces is enhanced; this process prevents the formation of transfer layer on the Al counterface. Above 400°C, the wear rate decreases because in this temperature, graphitization process enhances the transformation of sp$^3$ to sp$^2$ type bonding. Konca et al. investigated the wear characteristics of the non hydrogenated DLC coating at elevated temperature. They investigated wear rate of the deposited material, which is tested at 25°C, annealed at 300°C, and tested at 25°C temperature. The last sample is as-deposited, which is tested at 300°C. All the experimental samples are prepared at a negative bias voltage of 80 and 60 V. They found that the annealed sample has a higher wear rate than the as deposited sample at room temperature, because a
coating surface oxidation occurs during the annealing process. This hypothesis is proven by the EDS result. The result showed that the annealed sample has a higher oxygen percentage. The comparison of the as-deposited DLC coating tested at 25°C and at 300°C showed that at higher temperature, wear rate is also higher. Veverkova et al.\textsuperscript{161} showed that with increasing temperature, wear coefficient is also increased at different load and number of rotation (Figure 8). According to Figure 8, the wear coefficient is higher for 10 cycles for both loading conditions. However, with increasing time, wear rate decreases because the wear mechanism is initially abrasive. Krumpiegl et al.\textsuperscript{162} tested the friction and wear behavior of a-C, a-C:H, and Ti–C:H in a vacuum chamber and air-exposed environment at 450°C. They found that in a vacuum chamber, no loss of hardness is observed after testing. However, in the case of air-exposed environment, significant loss of hardness occurs because of oxidation.

At elevated temperature, DLC film gradually transforms from highly disordered structure to an ordered structure. During deposition, the films form an unstable phase; and upon exposure to thermal energy, these films tend to re-orient their structures.\textsuperscript{97,163} In the case of hydrogenated DLC film at elevated temperature, some of the unbounded hydrogen atoms diffuse out and leave a porous structure in the film. Therefore, with change of such chemical and structural morphology, wear and friction behavior also changes.\textsuperscript{90} The end product after exposure to elevated temperature may be highly porous and may produce a graphitic thin layer that is very soft, which wears out quickly. Compared to hydrogenated DLC film, non hydrogenated ta-C type film have higher endurance limit at elevated temperature.\textsuperscript{60}

2.5.3. Doping

In general, doping enhances wear property. As a dopant, some metals (e.g., Fe, Cr, W, Ti, Cu, Au, Al, Ag, and V) and non metals (e.g., Si, N, B, O, and F) can be used to enhance wear property.

2.5.3.1. Silicon-containing DLC. Ikeyama et al.\textsuperscript{99} used Si as a dopant and an interlayer to promote adhesion and tribological characteristics. In their experiment, they incorporated Si by flowing tetramethylsilane (TMS) gas. By increasing the flow rate, the Si concentration in the coating increases. They also found that wear rate decreases until the increment of TMS gas flow does not reach 1 sccm. Furthermore, with further increment of gas flow, the wear rate of the coating increases, although friction coefficient decreases. A relationship is noted between the amount of wear debris and hardness value. A rapid drop of hardness is observed within the TMS flow rate from 2–3.5 sccm, and as a result, wear rate also increases.

Wu et al.\textsuperscript{164} investigated the tribological characteristics in water of Si–DLC coating. Their investigation showed that increasing Si content decreases the wear of the counter face, but increases the wear of coated surface. In water environment, some tribochemical reaction occurs. Such reaction is responsible for the low wear of the counter face. SiOx(OH)y gel is formed on the counter face. The sliding contact surface is mostly chemically stable. Therefore, this surface has little attraction towards outside species under static conditions. However, in dynamic sliding condition, these surfaces can interact with counter faces and gaseous molecules in their surroundings. In doped condition, the probability of this type of interaction increases. Depending on the nature and extent of such interactions, a severe fluctuation is observed in the friction and wear behavior of DLC coating.\textsuperscript{165,166} Reactivity of the doping element with oxygen or humidity during sliding may result in higher inertness of the carbonaceous network. For example, Si incorporation forms silicon hydroxides during the test. As a result, CoF and wear rate can be less sensitive to the relative humidity.\textsuperscript{161,167}

2.5.3.2. Fluorine-containing DLC. Grill et al.\textsuperscript{168} prepared fluorinated DLC films by d.c. PACVD from pure difluorobenzene (DFB) or hexafluorobenzene (HFB) with various dilutions. The films deposited from DFB contained less than 10 at% fluorine and had a wear resistance similar to that of non fluorinated DLC. The film that is deposited from HFB contained 45 at% fluorine. This film is very soft and has no wear resistance. Diluting the precursor (HFB) with Ar reduced the fluorine concentration in the film; however, this process had did not increase the wear resistance. By contrast, dilution

FIG. 8. Wear coefficient vs. temperature for 7 and 10 N applied normal loads. (© Elsevier. Reproduced with permission of Veverkova and Hainsworth.\textsuperscript{161} Permission to reuse must be obtained from the rightsholder.)
with hydrogen increases the wear resistance of F–DLC film. Donnet et al.\textsuperscript{166} deposited a-C:H:F films by r.f. PACVD from HFB diluted with hydrogen. Average impact energy of the ions on the growing film has a significant function in controlling the film wear rate for a given dilution mixture concentration. Comparable wear rate with non fluorinated DLC has been found for the film, which contains 20 at% fluorine and 10 at% hydrogen. The highest wear resistance was achieved for films deposited at the highest deposition bias and lowest gas pressure. These films exhibited a more cross-linked structure with a lower fraction of unbound fluorine and higher compressive stresses, compared to less wear-resistant films. In addition, micro-wear of a-C:H:Si can be reduced by fluorination.

Jaoul et al.\textsuperscript{170} investigated the tribological characteristics of fluorinated a-C:H:F DLC in dry conditions. They found a significant improvement in wear resistance compared to a-C:H-type DLC. Moreover, fluorination led to a shorter run-in period.

2.5.3.3. Nitrogen-containing DLC. Nitrogen incorporation in the DLC film increases the sp\textsuperscript{2} fraction in the coating structure. CN\textsubscript{x} coating has some inherent property of better durability and reduced internal stresses. As an outcome, wear rate becomes lower. Zou et al.\textsuperscript{171} investigated the wear rate variation at different nitrogen content, and found that wear rate decreases as the nitrogen content increases in the CN\textsubscript{x} coating structure. Kato et al.\textsuperscript{172} investigated the effect of compressive stress on the wear resistance of CN\textsubscript{x} coating. They suggested that high compressive stress reduces the wear rate of CN\textsubscript{x} coating. Alternately, tensile stress inside the coating favors the wear of the coating because tensile stress enhances crack propagation.

Cutiongeo et al.\textsuperscript{118} added nitrogen to the a-C:H DLC in a protective overcoat of magnetic thin film disks, which results in an improved wear resistance. The benefit of N doping to the DLC is difficult to describe because the properties of N-doped DLC largely depend on deposition condition, nitrogen content, as well as chemical and microstructural aspects.\textsuperscript{106}

2.5.3.4. Metal-containing DLC. Wang et al.\textsuperscript{138} investigated the tribological characteristics of Ti–DLC coating as a function of Ti target current. Compared to the Ti-free DLC coating, Ti–DLC coating shows better tribological characteristics because Ti incorporation generates Ti–C bond in the Ti–DLC coating when deposited in 0.5 A target current. In this target current, Ti–C bond formation deforms the carbon network\textsuperscript{139} and restricts the sliding in the grain boundary by limiting the intergrain space. Therefore, hardness increases and CoF and specific wear rate decreases. With the increment of target current to 1 A, Ti concentration increases and enhances formation of TiC second phase. By further increase of Ti target current, TiC second phase generation increases and results in a negative effect on the mechanical properties of Ti–DLC coating. This process also promotes the graphitization of Ti-DLC coating. High Ti content in the coating surface enhances Ti oxidation during sliding because heat is generated at this time. In humid environment, high percentage of TiC second phase cannot be shielded because water molecules saturate sp\textsuperscript{2} bonding and soften the DLC layer; thus, wear rate increases.\textsuperscript{173}

Fu et al.\textsuperscript{174} investigated the tribological characteristics of W–DLC in ambient condition and poly-alfa-olefin (PAO) lubricated condition. In ambient air, wear rate has been found to decrease up to a W content of 3.08%. Further increment will cause the gradual increment of wear rate. However, in PAO-lubricated condition, wear rate was found to be steady up to a W content of 10%. Further increment will cause a gradual increment of wear rate in PAO-lubricated condition. Tungsten content up to 3.08% will greatly improve the coating toughness and the adhesion with the substrate. Further increment will increase the appearance of more free W phase and WC phase in the coatings. As a result, adhesion between the contacting surfaces increases, which causes adhesive wear of the surfaces. Some studies have shown the tribological characteristics of W–DLC in dry condition.\textsuperscript{175–177} Some improvement in adhesion has been found to further enhance the wear properties of W–DLC coating.

Recently Zou et al.\textsuperscript{178} investigated the effect of Cr concentration on structure, hardness, and high temperature tribological application. They also compared the results with non doped DLC. The tribology test was performed at 400°C. The results show that the non doped DLC failed after certain period of time with high CoF. However, Cr-doped DLC can sustain without failure within the same period with a stable CoF. Comparative low stress and comparable hardness is the key point to enhance the wear resistance of the Cr–DLC. Chang et al.\textsuperscript{141} investigated the wear characteristics of Ti–DLC, Zr–DLC, and Cr–DLC, and observed the lowest wear rate in the Cr–DLC. Cr–DLC exhibits highest sp\textsuperscript{3}/sp\textsuperscript{2} bond ratio; therefore, highest hardness has been achieved, as well as lower internal stress because of metal doping. These changes eventually results in lower wear rate. Singh et al.\textsuperscript{179} investigated that Cr percentage more than 12 at% showed an adverse effect on the wear resistance because incorporation of more than 12 at% Cr results in carbide particle formation, which adversely affect the wear resistance of coating.

Some studies have been conducted to investigate the doping effect on tribological characteristics, such as Ta doping,\textsuperscript{84,180} Nb doping,\textsuperscript{181,182} and Zr doping.\textsuperscript{51,183} The main benefit of metal doping is that this process decreases the internal stress that further increases wear resistance.

2.5.4. Sliding Velocity and Load

Wear rate decreases as the normal load increases. With the increment of sliding velocity, wear volume increases up to a certain value of sliding velocity and eventually decreases with…
further increment of velocity (Fig. 9a). Kim et al.\textsuperscript{145} investigated the wear rate fluctuation of both surfaces with increasing sliding velocity and normal load. They found that at constant sliding velocity, with the increase of normal load, the average wear rates of DLC coatings and AISI 52100 steel balls decrease. Furthermore, the average wear volume of the two mating surfaces increase. Alternately, when they increase the sliding velocity with constant load, the average wear rates and wear volumes of both surfaces increase up to a maximum value, which then decreases with increasing sliding velocity. Figure 9a shows the DLC coating wear rate changes. Degree of transfer layer formation has an important function for these types of wear rate and volume fluctuation. The degree of transfer layer formation generally increases with the increase of sliding velocity and normal load. At constant normal load, with increased sliding velocity, wear rate and volume also increases; because in this velocity range, the transfer layer is not well formed. According to Eq. (1), with the increase in sliding velocity and normal load, flash temperature at contact asperities increases. Therefore, the degree of graphitization of the DLC layer increases, and the softening of the counter surface occurs with the increase of flash temperature.\textsuperscript{90}

2.5.5. Counter Face

Counter face has a direct impact on the wear behavior of the DLC coating. Table 4 shows the effect of counter face on the wear behavior of the DLC coating and mating surfaces at humid and dry conditions.\textsuperscript{149} Si\textsubscript{3}N\textsubscript{4} ball has a lower wear rate in dry condition compared to steel ball. However, when the condition is humid, the steel ball has lower wear rate compared to the Si\textsubscript{3}N\textsubscript{4} ball. Thus, some kinds of tribochemical reaction favored the wear property of the steel ball in humid condition. Veverkova et al.\textsuperscript{161} found that during the pin-on-disk test, steel versus W–DLC showed higher wear rate compared to W–DLC/DLC coating pair, which might be due to tribolayer formation in the counter faces. The formation of tribolayers is important in controlling friction and wear property.\textsuperscript{184} Water absorption ability of different counter face has different values. In addition, the materials that absorb water can lower the wear rate of the mating surfaces because of the lubrication effect of water layer.

2.6. Lubrication

Currently, DLC is considered as a promising non ferrous coating because of its excellent tribological characteristics. If DLC coating is applied in engine parts that are prone to heavy frictional power loss and hostile environment, then this coating can be protected by lubrication. Lubricating oil will isolate the coating from surrounding hostile environment and can function as a coolant to keep the temperature within the allowable limit. Lubricants are by far formulated to function with ferrous materials; therefore, lubricant additive interaction with non ferrous materials should be discussed. Some contradictions arise in this matter. According to Kano and Yasuda,\textsuperscript{185} no stable tribofilm is found on the DLC surface when an additive is used, whereas other research groups have proven the tribofilm formation on DLC surface.\textsuperscript{186,187} Tribofilm formation also depends on some physical properties of DLC coating, such as dopant utilization and hydrogen content.

Hydrogen stabilizes the random covalent network of DLC coating and prevents this network from graphitization. Lubricant works as a coolant; when this substance is added, the contact temperature remains within the allowable range. Therefore, graphitization will not take place. As a result, tribochemical interactions of DLC and additives become dominant. Some researchers found that a-C DLC provides low CoF than a-C:H DLC in lubricated condition. Higher surface energy leads to better interaction with a-C:H DLC. Surface energy is low for a-C:H because of the difference in their molecular structure. When high temperature is generated during the sliding friction in contact, sp\textsuperscript{2} to sp\textsuperscript{3} conversion of the bond takes place. This sp\textsuperscript{2} bond type represents the graphite-like

FIG. 9. Wear volume (a) and wear rate (b) of DLC coating at different load and velocity. (© Elsevier. Reproduced with permission of Kim and Kim.\textsuperscript{145} Permission to reuse must be obtained from the rightsholder.)
Pronounced in the case of a-C DLC. Some conflicts about passivated by lubricant additives; thus, tribofilm formation is toward lubricant additives. For a-C, the active sites can be hydrogen atoms. Therefore, this material shows lower reactivity. In the case of a-C:H DLC, these active sites can be passivated by hydrogen atoms. Therefore, this material shows lower reactivity towards lubricant additives. For a-C, the active sites can be passivated by lubricant additives; thus, tribofilm formation is pronounced in the case of a-C DLC. Some conflicts about this matter has been reported, although some researchers showed the positive effect of hydrogen. Bouchet et al. found in their observation that in the presence of MoDTC and ZDDP additives, a-C:H showed better friction property compared to a-C. MoDTC and ZDDP showed better reactivity with a-C:H. Based from XPS tribofilm analysis, MoS2/MoO3 ratio is found to be five times higher than the tribofilm formed by a-C DLC coating. The importance of MoS2/MoO3 ratio will be discussed in Section 2.6.3.

Ferrous and non ferrous substances can be doped in DLC to obtain some physical and mechanical improvement. When the condition is lubricated, metal-doped DLC have some special reactivity. Metal-doped DLC forms metal carbide and improves DLC film strength. Boundary lubrication can be improved if high strength carbide is formed in the defective part of cross-linked carbon network of DLC coating. Kalin et al. investigated the tribological behavior of steel/steel, steel/a-C:H DLC, steel/W–DLC, and self-mated DLC/DLC for both W doped and non doped condition in different lubricated conditions. The results of their experiment are shown in Fig. 10. By comparing the results when lubricated with mineral oil and sunflower oil, Figures 10 and 11 show that sunflower oil provides better property because this substance has large amount of unsaturated molecules and polar components. Steel–steel contact has the lowest wear irrespective to the base oil type. Wear rate also decreases when additives are added. Some kinds of tribo-chemical interaction promote tribofilm formation in the mating surface. Steel–steel contact has greater surface energy compared to at least one contact with DLC coating. Therefore, tribofilm formation in both mating surfaces reduces friction and wear property. Wear rate decreased when they tested the W–DLC/W–DLC and a-DLC/a-DLC mating surfaces in presence of additives. In the case of W–DLC mating surface, W helps in tribofilm formation since W is a reactive metal. For the a-DLC/a-DLC mating surfaces, the adhesion is lower. Although these materials are inert towards the lubricating oils and additives, the friction and wear rate is quite low.

Kalin et al. investigated the function of base oil polarity and saturation characteristics in the tribological investigation of the a-C:H coating lubricated with natural and synthetic biodegradable oils. Figure 12 shows the fatty acid saturation level of different fatty acids. Non saturated fatty acid is good for better lubrication, and saturated fatty acid is good for better oxidation stability. Therefore, if better oxidation stability is needed, fatty acid lubrication should be sacrificed. Figure 13a shows different types of acid that are found in different types of biolubricant. This figure also shows the molecular structures of these acid types. Figure 13b shows the conventional boundary lubrication mechanisms. In this mechanism, adsorption of oils and additive polar groups at the oxidized metal surface takes place. Thus, higher number of polar groups in a component results in better tribological characteristics in metal tribosystems. Most metal lubrication mechanism is based on the physiabsorption or chemiabsorption of polar groups from the oil and additive onto the oxidized metal surface. In addition, most of these mechanisms occur through chemical reactions between the additives and the reactive clean metal surfaces under high stress and high temperature conditions. This is the major drawback of DLC coating when used in lubricating media.

Figure 12 shows the order of lubricating property and oxidation stability with respect to different types of oil. In this study, oils are arranged according to their saturation level. Using additives, wear rate decreases significantly. This behavior suggests that additive might function in minimizing the adhesion between the mating surfaces. Therefore, additive and mating surface interaction is important in minimizing the friction. Different types of additive are added to enhance the friction and wear property, as listed in Table 5.
2.6.1. DLC–Extreme Pressure (EP) Additive Interaction

EP additives are additives for lubricants, which have a function in decreasing the wear of the parts of engine components exposed to very high pressures. Therefore, the coating to the engine components, which is exposed to high pressure might have the possibility to interact with EP additives. Thus, the study of EP additive to different types of DLC coating interaction has become important. Non doped DLC is comparatively inert towards the additive coating interaction. However, when this material is doped with metal, some interactions take place between the DLC and the additive because metal has higher surface energy. Some studies on the tribological characteristics of steel/DLC contacts have been conducted. Kalin et al. investigated the interaction of metal-doped (Ti, WC) DLC with EP additive in tribological and static condition. They investigated the wear and friction property of metal doped, non doped, and steel self-mated contact in the presence of mineral oil and additive-added mineral oil. In each case, additive-added mineral oil shows lower wear rate; however, no significant change of friction property is observed. The change of wear rate is greater for metal-doped DLC coating. Non doped hydrogenated DLC coating shows low friction in the absence of additive. However, oil additive blend shows higher friction because in the presence of additive, a viscous tribofilm is formed in the non doped hydrogenated DLC coating surface and this oil additive hinders the motion. Through this reaction, friction increases, but wear property enhances because the tribofilm protects the coating layer. For uncoated steel surface, maximum wear causes adhesion when tested in oil-lubricated condition. However, when additive is added, adhesion is minimized. Same case is true for metal-doped DLC coating. In every case, tribofilm formation takes place; therefore, different degrees of reactivity are observed among different coating surfaces. Kalin et al. showed that Ti-doped DLC coating have high reactivity compared to WC-doped DLC and non doped hydrogenated DLC coating. They observed a difference in phosphorus/sulfur (P/S) ratio after the friction and wear test in the worn surface.
by XPS analysis. P and S come from the additive (EP), the ratio in the additive components is 0.5 (P/S) as shown in Table 4. However, in the worn surface, the ratio is changing because of some reactivity towards the surface. Ti-doped DLC worn surface have 10 times higher P/S ratio compared to the other tested coating surfaces. Oxide formation is actually important. Ti has a higher reactivity with oxygen and forms TiO and TiO₂. TiO₂ is the most stable phase of the Ti compounds. Friction heating enhances TiO₂ formation and some oxygen vacancies are also present in the crystal structure; therefore, the vacant sites function as hotspots for the reaction with EP additive.¹⁹⁹

In another article, Kalin et al.²⁰⁰ described the contact temperature effect on the reactivity of the oil additives with DLC coating. Contact temperature can significantly differ from the test temperature because of frictional heating. Addition of EP additive to the base oil at different temperatures affects the friction and wear property differently. They tested the materials at different testing temperatures and found that at 80°C, the wear is minimized compared to the base oil by about 40%, and at 150°C by about 65%. Therefore, the reactivity of additive increased with temperature. The opposite behavior is observed in the CoF. Therefore, if the main target is to minimize the wear, then EP additive is effective, but only in elevated temperature. Some chemical changes have also been observed because of the addition of EP additive at 150°C, which forms phosphates and organic sulfur or sulfates in the DLC surface. The reactivity is quite different from the reactivity with metal surface because EP additive needs more time to react with DLC coating. In addition, the reaction activation temperature is close to 250°C (contact temperature). Kalin et al.²⁰⁰ showed that contact temperature is slightly above the testing temperature. Although the contact temperature is close to the graphitization temperature, graphitization does not take place because the additive protects the coating from graphitization. Mistry et al.²⁰¹ described the tribochemical reaction of WC-doped DLC coating in EP lubricated condition. The commonly used EP additives are sulfur based and phosphorus based. They investigated the relative amount of different elements present in the tribofilm within the run-in period and at steady state condition. They found that at steady state, the amount of elements coming from additives was considerably increased, compared to the run-in period. Thus, reactivity increased with time, and tribofilm thickness increased as well. As a result, wear rate also decreased.
2.6.2. DLC–AW Additive Interaction

ZDDP additive shows great anti-wear properties. Therefore, some studies have been conducted to determine the surface protection mechanism. ZDDP additive is specially made to interact with the steel surface. Therefore, some question arises in the absence of steel surface; whether this material is still capable of forming tribofilm or not. DLC coating is inert compared to the metallic surface. Thus, DLC coating cannot interact in a manner similar to that of the metal surface. Therefore, some studies have been performed to investigate the DLC behavior under oil-lubricated condition.8,16,158

Vercammen et al.202 investigated the tribological performance of non doped DLC and doped DLC against metal under boundary lubricated condition. They used 1% AW additive with the base oil (unsaturated ester and saturated ester), and found that DLC coating reduce the wear in lubricated condition. However, AW additive introduction is more beneficial for steel/steel contact than for DLC/steel contact. Therefore, the coating properties can actually reduce the wear rate significantly than the additives in the lubricant. For doped DLC, AW additive has limited functionality in minimizing the friction compared to DLC tested with EP additive. Therefore, the AW additive has lower reactivity to the metal compared to EP additive.

Vengudusamy et al.203 investigated the behavior of ZDDP additive when used in six types of DLC coating both in self-mated and DLC/steel counter face. In ZDDP solution, DLC/steel combination shows slightly higher friction value compared to DLC/DLC contact. This finding resulted from the negative effect of tribofilm on the steel surface. Higher force is required to overcome the shear stress of tribofilm; thus, the CoF value is higher for DLC/steel combination. After 2 h of testing, every tested combination surface shows evidence of tribofilm formation. The surface contains P, S, and Zn. Elements come from ZDDP additive. Their analysis shows that steel surface reacts very fast; thus, immediate tribofilm formation is observed. However, DLC-coated surface requires more time to produce a tribofilm. Additional factors, such as temperature and load, can influence the reaction kinetics. Higher temperature and pressure accelerate the tribochemical reaction.

Equey et al.16 investigated the difference in friction between DLC/DLC and steel/steel contacts in base oil and base oil + ZDDP additive lubricating media. As base oil, they used PAO oil. They found that the addition of ZDDP additive in steel/steel contact decreases the CoF. Opposite result was found in case of DLC/DLC contact. However, DLC/DLC contact shows better CoF compared to steel/steel contact when tested in base oil. This finding may be due to low shear strength of the DLC surface as a result of transfer film formation, which is the DLC characteristic as dry lubricant. The addition of ZDDP causes an increase in CoF, which indicates that ZDDP inhibits the formation of transfer layer because of tribochemical reaction or ZDDP adsorption on DLC surface.

2.6.3. DLC–FM Additive Interaction

Friction modifier (FM) additives have some beneficial effects to improve the friction and wear property of DLC-coated parts. Moly-dimers (MoDTC) and trimers are commonly used as friction modifiers. Miyake et al.187 described the interaction of MoDTC additive with DLC coating doped with metal dopants (e.g., Ti, Fe, Mo) at different concentration levels. They made a comparison with the non doped DLC and doped DLC at varying amount of dopant metal component. The lubrication effect of oil-containing MoDTC is negligible in the absence of metal dopant in the DLC coating. Therefore, lubrication effect of non doped DLC is quite similar to the Si substrate. Thus, coating can only be effective if metal is added as a dopant because metal-containing DLC has active sites that react with additives. The reaction also takes time; thus, at the initial stage, CoF is high and gradually decreases because of tribofilm formation reaction.

Haque et al.205 stated two structure types of the friction modifier additive; one is a moly-dimer (MoDTC) and another is a moly-trimer (Figure 14). Gossiord et al.206 described the formation mechanism of MoS2 from MoDTC. MoS2 leads to the reduction of friction. In addition, MoS2 has a layer-by-layer structure, and electrostatic repulsion force functions between the layers. Therefore, these layers can slide above one another easily. Oxygen that is present in the MoDTC structure has a detrimental effect on friction performance because during the MoS2 formation, another reaction takes place that form oxides. Therefore, moly-trimer has better friction property because of the absence of oxygen in the molecular structure. As evidence, they showed in XPS analysis of tribo film that the higher ratio of MoS2/MoO3 gives better frictional property.
Figure 15 shows the reaction mechanism of MoS$_2$ formation in the binary lubrication mechanism; in this context, ZDDP functions as a catalyst to promote MoS$_2$ formation.\cite{186}

Bouchet et al.\cite{186} investigated the tribological characteristics of DLC coatings in boundary lubrication condition, and related the properties with the hydrogen content in the coating. They used ZDDP and MoDTC additive and found that hydrogenated DLC can be better lubricated in presence of MoDTC. However, AW additive (ZDDP) cannot perform accordingly to reduce the wear rate. In this process, ZDDP functions as catalyst, as stated earlier.

2.6.4. DLC–Organic FM Additive Interaction

Some organic friction modifiers have strong influence in reducing the CoF of DLC-coated surface. Some studies have observed glycerol and glycerol mono-oleate (GMO). Research has already been conducted using these additives with PAO.\cite{207,208} Hydrogen content in the DLC structure has some strong influence on the interaction of these additives with DLC coating.\cite{209-211}

Kano et al.\cite{207} studied the effect of GMO friction modifier in presence of PAO of ta-C/steel, a-C:H/steel, and steel/steel tribocouples. They found that ta-C/steel tribopair showed ultralow CoF. The tribofilm formed on the steel surfaces because of tribochemical reactions. In addition, shearing of tribofilm results in increments in the CoF. The tribofilm formed on the hydrogen-free ta-C DLC coating of low shear strength, which causes low CoF. Friction-induced tribofilm exhibit a low CoF. They investigated that the ratio between OH$^-$ and GMO ion fragments has peak intensities both inside the tribofilm and outside the tribofilm. They also found that inside the tribofilm, the ratio increased. These phenomena also confirm the presence of friction-induced tribofilm in the wear region. They suggested the formation of friction induced hydroxylated-terminated carbon surface. This new surface chemistry is formed by the tribochemical reaction of lubricant alcohol function groups with the friction-activated ta-C atoms. Figure 16 shows the reaction mechanism of DLC with GMO additive. Tasdemir et al.\cite{212} suggested that the dangling bond created at the top surfaces of DLC, which is caused by friction and wear, easily react with environmental species (such as H$_2$O, O, and H) in dry sliding. In addition, the resulting terminated surface reduce friction significantly. Matta et. al.\cite{210} suggested that when sliding on the OH$^-$/terminated ta-C friction

![FIG. 14](image1.png)

**FIG. 14.** Molecular structure: a. Moly dimer and b. Moly trimer. (© Elsevier. Reproduced with permission of Kalin et al.\cite{205} Permission to reuse must be obtained from the rightsholder.)

![FIG. 15](image2.png)

**FIG. 15.** Electrochemical process of the MoS$_2$ formation from MoDTC. (© Elsevier. Reproduced with permission of Barros Bouchet et al.\cite{186} Permission to reuse must be obtained from the rightsholder.)

![FIG. 16](image3.png)

**FIG. 16.** Schematic view of friction induced hydroxylated-terminated carbon surfaces. (© Springer. Reproduced with permission of Kano et al.\cite{207} Permission to reuse must be obtained from the rightsholder.)
couples, glycerol decomposition and water and glycoaldehyde molecule formation in the interface occur. The water molecules that are formed by the interaction of glycerol with the surface OH groups by hydrogen bond cause low friction.

3. CONCLUSIONS

The following conclusions are based on published literature on DLC coating for tribological application to the parts that are prone to frictional power losses and severe wear during operation.

- Different types of DLC coating have different behaviors. In addition, hydrogenated DLC is better as dry lubricant because this material is softer than non-hydrogenated DLC. Therefore, hydrogenated DLC can easily form a transfer layer on the counter surface to enhance the friction property. However, hydrogenated DLC has an adverse effect under humid condition.
- The initial CoF in the run-in period is low compared with the mating parts, which are uncoated during the same testing. Therefore, an instant formation of transfer layer is found on the counter surface to reduce the abrasion resistance because initially, the dominant factor that hinders the sliding motion is abrasion.
- Metal doping is very beneficial in lubricated condition because metal forms oxide, and oxides are the active sites for lubricant additive interaction. Non-metals (such as silicon) are commonly used in humid condition because humidity helps in tribofilm formation to reduce friction.
- Extreme pressure and friction modifier additives have better lubricating property for DLC–DLC mating surface compared with anti-wear additives (ZDDP). However, when added to commercial lubricants, DLC–DLC contact has inferior frictional property compared with metal–metal contacts.

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