

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 sp^3/sp^2 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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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

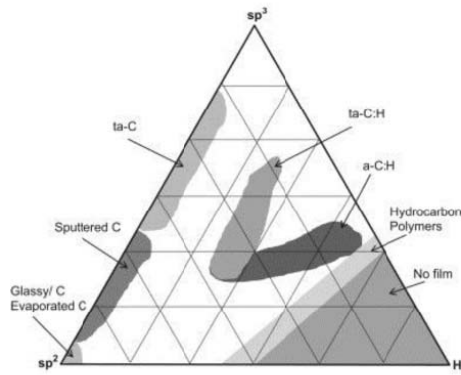


FIG. 1. Ternary phase diagram for various DLC films with respect to their sp^3 , sp^2 type bonding and hydrogen content in the structure. (© Elsevier. Reproduced with permission of Love et al.¹⁸ Permission to reuse must be obtained from the rightsholder.)

automotive valve train application,^{4,5} bearings,^{4,6} gears,^{7,8} piston rings,^{9,10} piston pins, direct-injection fuel systems, and cutting and forming tools.¹¹ 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,¹²⁻¹⁴ whereas some reports state absent or negative interaction with DLC¹⁵ (only for non doped DLC, interaction with MoDTC additive.^{16,17} 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,

TABLE 1
Friction coefficient and wear rate of different types of DLC coating in different environmental condition¹⁹

	Diamond coating	Non Hydrogenated DLC	Hydrogenated DLC	Doped DLC	References
Structure	CVD diamond	a-C ta-C	a-C:H ta-C:H	a-C:Me a-C:H:Me a-C:H:x sp^2 & sp^3	20-39
Atomic Structure	sp^3	sp^2 & sp^3	sp^2 & sp^3	sp^2 & sp^3	
Hydrogen content	—	>1%	10-50%	—	
μ in vacuum	0.02-1	0.3-0.8	0.007-0.05	0.03	
μ in dry N_2	0.03	0.6-0.7	0.001-0.15	0.007	
μ in dry air 5-15% RH	0.08-0.1	0.6	0.025-0.22	0.03	
μ in humid air 15-95%	0.05-0.15	0.05-0.23	0.02-0.5	0.03-0.4	
μ in water	0.002-0.08	0.07-0.1	0.01-0.7	0.06	
μ in oil	—	0.03	0.1	0.1	
K in vacuum	1-1000	60-400	0.0001	—	
K in dry N_2	0.1-0.2	0.1-0.7	0.00001-0.1	—	
K in dry air 5-15% RH	1-5	0.3	0.01-0.4	—	
K in humid air 15-95%	0.04-0.06	0.0001-400	0.01-1	0.1-1	
K in water	0.0001-1	—	0.002-0.2	0.15	
K in oil	—	—	—	0.1	

μ refers to coefficient of friction

K refers to wear rate [$\times 10^{-6} \text{mm}^3(\text{Nm})^{-1}$]

Me refers to metal, such as W, Ti, Mo, Fe, V, ...

X refers to nonmetal, such as Si, O, N, F, B, ...

TABLE 2
Different types of coating applied to engine parts

Engine component	Substrate	Coating	References
Valve	X20CrMo V121 steel	chromium carbide	40
	M2 tool steel	DLC	41
bearings	Stainless steel	chromium	42
	AISI 52100 steel	DLC	6
	100Cr6 ball bearings	(Cr,Al)N Cr ₂ N CrN + nC(nano sized carbon)	43–44
Gears	SCM420 alloy	Molybdenum disulphide/titanium (MoS ₂ /Ti)	45
	DIN 17210 20MnCr5 steel	W-DLC, DLC	8
	M42 steel	Carbon/Chromium (C/Cr) composite	46
	16MnCr5 and SAE4140 steel	thermal sprayed molybdenum	47
Piston ring	cast iron	Chromium ceramic	48
		DLC TiN TiAlN	
Piston pin	Stainless steel	chromium nitride	49
	AISI 440C steel	Al-Mo-Ni	50–51
	Aluminum Alloy 390	DLC	52
		CrN	
	Phosphatized coating		53
Direct injection fuel systems	52100 steel	WC/C coating	54
	Ceramic or steel	Ceramic coating	55
	AISI 52100 (UNS# G52986) steel	DLC near-frictionless carbon (NFC)	56

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. The processing techniques are also simply applied in a wide range of processing parameters. 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 non-metal 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, Erdemir⁵⁷ 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.

However, 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 frictional 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, π - π^* interactions and van der Waals forces. The π - π^* interactions are active between graphitic carbons, such as sp^2 -bonded carbon atoms of DLC films.

Some unbound σ bonds are present in the DLC contacting surface. The elimination of this bond type is important in minimizing 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 continuously 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, π - π^* 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 shielding by providing higher degree of passivation. Therefore, elimination of strong covalent σ bond and π - π^* interaction, as well as the possibility of obtaining di-hydrated carbon in the DLC are the major reasons for the superlubricity of hydrogenated DLC. In an air-exposed environment, increments of friction caused by capillary forces are noted around the real contact area. Capillary force increases because water molecules 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 hydrogen from the surrounding environment. When such surfaces are exposed to an inert environment, such contact cannot be passivated by environmental species. Therefore, fresh σ bonds and π - π^* interactions are enhanced, which results in higher friction in inert or vacuum environment.

2.1.2. Effect of sp^3/sp^2 Ratio

The sp^3/sp^2 ratio is an important factor that determines the tribological characteristics of different types of DLC coating. ta-C has the highest percentage of sp^3 content (80% to 88%) in its structure. In addition, sputtered carbon, which often

referred to as amorphous carbon (a-C), contains lowest amount of sp^3 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% sp^3 content in their structure, 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 sp^3 content in the structure. Higher sp^3 content percentage shows higher hardness value. Although soft a-C:H DLC has higher percentage of sp^3 content in its structure, this materials has decreased hardness. Sputtered carbon a-C coating has 5% sp^3 content and 15 GPa hardness.⁵⁹

Ronkainen et al.²⁹ investigated the tribological characteristics of ta-C and a-C:H DLC in dry environment. Although a-C:H and ta-C DLC have high proportion of sp^3 bonding in the structure, the transformation to graphitic structure is more pronounced 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 containing sp^3 bonding is more stable than the sp^3 bonding of a-C:H; therefore, graphitization rate is low in ta-C DLC. In addition, 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/a-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 linear 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 deposition. This technique can be employed to DLC coating for both hydrogenated and non hydrogenated condition. 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 electron helps 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 C_2H_2 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 $[\text{Fe}(\text{C}_5\text{H}_5)_2]$, cyclooctatetraenyl-iron-tricarbonyl $[\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3]$, methyl-cyclopentadienyl-iron-dicarbonyl $[\text{CpFeCH}_3(\text{CO})_2]$, 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

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