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A review of Influence of MoS_2 on the tribological characteristics of

diamond-like carbon coatings

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Abstract

Diamond-like carbon (DLC) coatings are increasingly used on machine parts due to their excellent friction and wear resistance. Therefore, it is important to formulate lubricants that can work effectively with these coatings. To do this, it is necessary to know how the various surface-reactive additives generally used in lubricants behave with DLCs. Tribological contacts (friction and wear) with solid lubricant coatings generally result in the transfer of a thin layer of material from the surface of the coating to the mating surface, commonly referred to as a transfer film or tribofilm. The wear surfaces may have different chemistry, microstructure and crystallographic texture than that of the main coating due to chemical reactions of the surface with the surrounding environment This article deals with the behavior of molybdenum dichalcogenide as a surface coating or as a filler in lubricating composites. The inherent lubricating lamellar structure of pure MoS is described, along with a brief summary of its wear and failure modes. Tribological performance of the DLC coatings, in combination with various base oils and lubricant additives, is analyzed by comparing their average friction and wear coefficient values, which have been calculated from published experimental data.

Keywords: Diamond-like carbon, tribology, lubrication, MoS2, Coefficient of friction

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1. Introduction

In recent years, many researchers and industrialists are engaged in the optimization and improvement of tribological properties for potential applications in surface engineering. Wear (tribological process) occurs when two surfaces contact and both/one move relative to each other [1-3]. A tribology study shows that even a 15-20% reduction in wear/friction can significantly reduce economic costs relative to environmental benefits. There are several tribological systems that offer ultra-low coefficient of friction, high wear resistance, and high mechanical properties [4,5]. Thin films of amorphous carbon are attracting growing interest due to their important properties such as extreme hardness, high electrical resistivity, optical transparency in the infrared region, and chemical inertness. Diamond-like carbon (DLC) coatings offer these properties and have been the subject of much recent research, which has shown that special care is required for optimal performance [6-8].

Although it is described as "diamond-like," DLC is actually not like crystalline diamond because it is black, not as hard, and virtually amorphous. Its microstructure allows for the incorporation of other species, and DLC comprises a family of such materials whose properties can be tailored far better than those of diamond [9-11]. Hydrogen is often present in amounts up to 40 atomic % and occupies regions of low electron density in the matrix. Its presence strongly influences the mechanical and tribological behavior of DLC coatings. Other commonly used additives include nitrogen, silicon, sulfur, tungsten, titanium or silver. Diamond-like carbon (DLC) coatings consist of C-C bonds of the sp2 and sp3 type and hydrogen moieties in varying amounts (Figure 1). The chemical and mechanical properties of DLC coatings vary considerably depending on their composition [12-14].

There are two subclasses of DLC films known as nonhydrogenated DLC films (tetrahedral amorphous carbon films (ta-C) and amorphous carbon films (a-C)) and hydrogenated DLC films (a-C:H). These films are composed of carbon and hydrogen atoms, with the carbon atoms forming mainly sp2 and sp3 hybridized bonds [15-17]. The ratio of sp3 and sp2 bonds is a crucial intrinsic parameter that determines the structure and properties of DLC films. DLC is intermediate in that it contains both types of bonds, and it is clearly harder and more brittle when the ratio of sp3 to sp2 is high. In mechanics, DLC coatings are mainly used for cutting tools and friction components that require good adhesion and tribological properties. High normal and shear stresses are the main causes of DLC failure, such as brittle spalling, abrasive wear and adhesive wear. Adhesive strength, coefficient of friction and wear rate are the most direct indices reflecting the properties of DLC coatings [3,18,19].

To improve the lubricating performance of modern engine lubricants, a complex package of additives is mixed into the base oil. One of the most important additives is a friction modifier, which reduces the coefficient of friction between two rubbing surfaces. One of the most commonly used is molybdenum dithiocarbamate (MoDTC) [20,21]. Molybdenum dithiocarbamate (MoDTC) is a well-known friction



Figure 1. The types of Diamond-Like Carbon (DLC)

modifier used for ferrous surfaces. With their low shear strength, MoS2 platelets derived from MoDTC decomposition provide low friction at tribological contacts under boundary lubrication conditions. The commonly used lubricant additives are designed to form tribofilms on iron surfaces. Therefore, it is important to optimize the compatibility of coating and lubricant so that additive solutions can be tailored to DLC surfaces [20,22,23].

Recently, the effect of MoDTC on increased wear of the DLC coating in a DLC/steel contact has been reported by the present authors and others. Several mechanisms have been proposed by which lubrication by MoDTC leads to high wear in tribological systems including DLC. Recent studies have shown that the interaction between MoDTC and the DLC coating often leads to a high wear rate despite the friction reduction achieved [21,24-26].

The objective of this work is to accurately investigate the chemical change of the surface of lubricated DLC coatings in the presence of MoDTC additives. To develop a better understanding of the interaction between DLC and MoDTC additive, the effect of lubricant degradation on DLC/steel contact was investigated. Particular attention was paid to DLCs, which exhibit completely different tribological behaviour.

2. Deposition Techniques

Deposition is known as a simple technique for fabricating a surface in order to create a layer(s) on it [27]. Surface uniformity, simple fabrication, decreased cost of production, and strange electrical, optical, and mechanical features are a number of diverse remarkable and beneficial properties that are provided by the coating deposition [28]. This procedure is mainly aimed at (i) depositing the conductive or insulating layers on a substrate, (ii) creating the local conductive channels used for the interconnection of devices, and (iii) constructing more complex structures in a single layer or multiple layers[29]. The deposition methods exist in a vast variety and are hugely different from one another. A great many of factors and criteria (e.g., the definite application and accessible resources) contribute to choosing a peculiar deposition technique[28]. The most common methods used for deposition consist thermal spray deposition, electrodeposition, physical vapor deposition and chemical vapor deposition (Figure 2)[30].

2.1 Thermal spray deposition

Thermal spray is a deposition technique with a number of coating processes. These processes comprise the deposition of fine-particled metallic or nonmetallic materials in a molten or semi-molten condition for making a coating. Materials such as powder, ceramic



Figure 2. Systematic diagram of deposition techniques

rod, wire, or molten materials can be used for coating. Thermal spray technique is useful for coating a large number of materials. The common application of thermal spray method is to provide functions like ear resistance, corrosion resistance, bioactivity and dielectric properties to materials [28]. The deposition process features generate coatings with distinctive microstructure that differ from traditional materials. With a high deposition rate, this method is applied for coating thick surfaces at a low budget [31]. Determining the hardness, porosity, bond strength, oxide content and surface roughness of the deposition helps to assess its quality. The temperature range in this method makes possible the coating of a large number of materials with rapid deposition rate. The categorization of thermal spray processes consists of combustion spray, plasma spray and cold spray. Combustion spray techniques are Detonation Spray (DS), High-Velocity Air Fuel (HVAF) or High-Velocity Oxy-Fuel (HVOF) and Flame Spraying (FS). Similarly, plasma spray processes are Plasma-Transferred Arc (PTA) deposition, Wire Arc Spraying (WAS), Radio frequency (RF) Induction Plasma Spraying, Atmospheric and controlled atmosphere plasma spraying (Figure 3) [30,32].

2.2 Electro-deposition

Electrodeposition is another technique for the deposition of an expansive range of two- and threedimensional materials at low cost. The principles of electrochemical phenomena connected with the reduction or deposition of electroactive and

accompanying species on the cathode surface are the basis for this method (Figure 4) [33]. The process of electrodeposition is carried out at a high rate and has the capacity of coating complex materials and controlled nanoporous coating. This method is a fresh coating method owing to its ability of controlling the costing microstructure and nanostructure, besides morphology and mineralization by different factors such as deposition potential/current, bath composition, temperature, and deposition time. However, this technique also suffers a number of drawbacks such as the need for the optimization of process parameters in each workpeice in order to achieve uniform thickness. Moreover, the acidic, alkaline, and cyanide discharge in the environment is also another issue [30,34]. In general, electrodeposition is categorized into direct current (DC) and pulse electrodeposition [35].

2.3 Physical vapor deposition

The application of physical mechanisms to form a condensable vapor followed by the depositing this material onto a substrate as a thin film or coating is known as the Physical vapor deposition (PVD). In this method, the material is atomic and extracted from a bulk source via heat, plasma, laser, ions, electrons, or other energy sources. The process contains the physical discharge of atoms or molecules from the source and their transfer onto the substrate surface by means of a vacuum or low-pressure environment [36]. Following their conveyance onto the substrate surface, atoms are condensed and nucleated. This process if applied for depositing film thickness ranging from



Figure 3. Thermal spray deposition techniques: (a) Wire flame spray, (b) plasma spray

nanometers to micrometers. The method features include low deposition rate and high cost and is useful for coating complex materials. Physical vapor deposition consists of evaporation, sputtering, and ion plating [29,30].

2.4 Chemical vapor deposition

CVD uses chemical reactions of a precursor gas in an activated heat, light, or plasma environment with the workpiece [34]. The resulting products are deposited on the surface of the substrate in the thin layers. Materials including metals, alloys, intermetallic, boron silicon, borides, silicides, carbides, oxides, and sulfides can be deposited with CVD [28]. This process is associated with temperature, pressure, mass. momentum, and energy transport. Several factors including type of substrate surface, vapor species, and concentration of vapor species effect on the film thickness deposition. The chemical reaction occurring in the CVD process are namely oxidation, reduction, pyrolysis, disproportionation, and reversible transfer. This technique is the most common deposition method for creating highly crystalline and highly hydrogenated carbon-based coatings [30,36]. CVD features are low deposition rate, high cost and it is used for coating thin films. CVD types include Atmospheric Pressure Chemical Vapor Deposition (APCVD), Low-Pressure Chemical Vapor Deposition (LPCVD), Metal Organic Chemical Vapor Deposition (MOCVD), Plasma Enhanced Chemical Vapor Deposition (PECVD), Laser Chemical Vapor Deposition (LCVD) [28].

2.5 Deposition mechanisms

The coating deposition is used to enhance mechanical, optical, thermal and tribological properties of materials. It is firstly important to present an appropriate approach into the system in order to improve mechanical, frictional and wear properties of substrate material under typical test conditions. To develop suitable interfacial bonding between film and substrate material a standard metallographic technique must be applied. In the mechanism of DLC/CNTs coating, to eliminate the surface roughness, the substrate material is cut and ground by 80-4000 grade emery paper. The substrate material is then varnished by 1/0, 2/0, 3/0 diamond paste cleaned with wood alcohol, ethanol or acetone. Following the cleaning of substrate material, for the purpose of extending the adhesive force between the substrate material and film, an additive film of Si ion, Ti /TiN/Cu is deposited on the substrate under working temperature. During DLC/CNTs deposition process, Ag or N₂ is repeatedly supplied for eliminating and preventing surface from contamination [30].

2.6 Deposition parameters

Different procedures with wide ranges of deposition parameters can be applied for depositing DLC coatings [37]. The managing parameters for most of the deposition methods include the cleaning treatment, arc current, pressure, time, deposition rate, substrate temperature and gas supply. Diamond-like carbon



Figure 4. Schematic diagram of the electrodeposition system.

coatings are believed to be one of the hardest coatings. One of the most favorable deposition methods is found to be Plasma-Assisted Chemical Vapor Deposition (PACVD). The varied parameters in the deposition is the factor that makes it possible to provide a unique vast range of materials and structures in a costly and environmentally friendly way [30,38].

3. Major types, properties and tribological behavior of carbon based caotings

Carbon-based coatings have recently used in many industries such as cutting tools, M/NEMS, biomedical, and automotive. This is mainly due to their impressive properties namely their superior hardness, wear resistance, chemical inertness, exceptionally low thermal expansion, and extremelylow friction, and especially their tribological applications. These coatings are generally composed of pure carbon, metal-doped carbon, and metal carbide (M-C) [28,39].

3.1 Pure carbon

As subcategories of pure carbon coatings, a-C and diamond-like carbon (DLC) coatings have been the subject of numerous studies due to their superior properties, such as low friction coefficient, high wear resistance, stability to environmental species, chemical inertness, mechanical hardness, optical transparency, and electrical conductivity [40,41].

3.1.1 H-free a-C or DLC Coatings

The superior mechanical and chemical properties of Diamond-like carbon (DLC) as a protective coating in

many fields have made it a worldwide attraction. In line with the industry's growing need for wearresistant tribological coatings, DLC coatings have proven to be highly effective solutions for components subjected to intense tribological conditions. The DLC or H-free a-C coatings can be considered as lowfriction and highly wear-resistant substances [28,42].

3.1.2 Hydrogenated a-C (H-DLC) Coatings

The nature of the DLC coating, whether it is hydrogenated or not, is an important factor in its tribological behavior. The role of hydrogen is crucial as it determines the tribochemical interactions between solid surfaces [42]. The effective prevention of C–C bonds at the frictional interface by the hydrogenbonded molecules on the DLC-coated surfaces leads to a significant reduction in the friction of theDLC coatings [28,43].

On the surfaces of highly hydrogenated DLC coatings, the carbon bonds and H atoms meet, which improves the weaker interaction on the surfaces and leads to a significant reduction in contact stress. However, due to the extreme temperature conditions, sliding speed, and moisture content, the chemical reactions would proceed and increase the friction coefficient. Many advances have been made in the development of H-DLC coatings and their processes to improve their tribological behavior [28].

3.1.3 ta-C coatings

Tetrahedral amorphous carbon (ta-C) is the hardest type of DLC coatings and can be both hydrogenated (a-C:H and ta-C:H) and non-hydrogenated (a-C, and

ta-C). Numerous dangling bonds result in a lower coefficient of friction in the ta-C coatings with 81% of the sp3 hybridized carbon resulting in a lower frictional force under lubricated conditions. The formation of the tribofilm and the week interactions between the two OH-terminated ta-C coatings and the lubricant provide extremely-low friction under lubricated conditions. At lower temperatures, the ta-C coatings are stable and exhibit excellent tribological properties, at high temperatures, however, a number of cracks develop and the coating dissolves [28,42,44].

3.2 Metal-doped carbon coatings

Metal-doped carbon coatings are generally consisting of nanoscale metal carbide particles implanted into the a-C matrix. The doping concentration has a strong influence on the structural and tribomechanical properties of the coatings. In such Me-DLC coatings, the ratio of carbon is in the range of 0.1–0.2. These hard coatings not only exhibit low friction under dry conditions, but also reduce compressive stress compared to undoped coatings [45,46].

One of the most practical means of improving the overall function of a-C coatings is to dope the a-C coatings with certain elements. The integration of elements can significantly improve a number of properties such as internal stresses and corrosion resistance. Metal-containing amorphous hydrocarbons (M-C:H) with 15 at % . metal (e.g. Ta, W, Ti or Nb) or less and a-C:H have nearly similar wear resistance and coefficient of friction. However, the electrical conductivities of M-C:H are many times higher. Residual stresses in a-C coatings can be released by the contribution of metal doping. In addition, the electrical conductivity and durability of pure a-C coatings can be improved by specific bonding states or nanocry stalline carbide, which are usually observed in doped a-C coatings [47-49].

3.3 Metal carbide coatings

Metal carbide coatings can be used as wear-resistant coatings in the automotive, biomedical, and cutting tool industries, as thermal barrier coatings in fast breeder test reactors, and as diffusion barrier coatings in the semiconductor industry [50,51]. The wide range of application of transitionmetal carbide (TMC) coatings in mechanical engineering includes improving the wear resistance of friction couples , reducing friction, and developing corrosion resistance and electrical conductivity [52].

increasing the metal content increases the amount of metalcarbide phase, resulting in a significant increase in hardness and elastic modulus. However, increasing the metal content dose not significantly affect the size of the carbide [53]. This is because the performance of the coating components is strongly influenced by the composition of the carbides, the type and percentage of binders, and the process parameters [54].

The development of hard nanocrystalline TMC phases embedded in an amorphous carbon (a-C) matrix to develop self-lubricating and high-performance wear resistant coatings has received remarkable research attention. The grain growth of the TMC phase is limited by the presence of the a-C matrix. Consequently, the mobility of plastic deformation during solid-state interactions is inhibited and wear resistance is enhanced. Moreover, TMC:a-C:H microstructures are formed during the reactive deposition process and the mechanical and tribological properties of the hard coatings improve significantly [51].

4. Tribochemical Behaviour of Machine Elements Having DLC and Lubricated with MoS₂

MoS₂ belongs to the transition metal dichalcogenide family represented by MX₂. In appearance and feel, molybdenum disulfide resembles graphite. It exhibits a lamellar structure with low shear strength in the direction parallel to the basal planes (Figure 5), which is due to mechanical anisotropy [55,56]. The anisotropy is caused by strong covalent bonds along the planes and weak van der Walls forces across the planes, which allows these planes to shear easily. However, a major drawback of MoS₂ is that it is highly reactive to water vapour and oxygen in the environment [57,58]. Under these conditions, formation of MoO₃ usually occurs, which is quite abrasive below 500 °C. Nevertheless, MoS₂ has always been preferred in space applications due to its extremely low friction in vacuum [59].

$$2 \operatorname{MoS}_2 + 7 \operatorname{O}_2 \longrightarrow 2 \operatorname{MoO}_3 + 4 \operatorname{SO}_2$$

Espejo and et. al [60] focus on the tribochemistry of molybdenum dithiocarbamate (MoDTC) as an oil additive to improve the frictional behavior of DLCcoated systems lubricated at the interface. The a-C:H



Figure 5. Mo complexes for catalyst precursor

coating lubricated with BO +MoDTC (base oil) leads to high wear of the coating. In this system, the presence of the molybdenum additive leads not only to the formation of MoS₂, but also to the formation of large carbonaceous deposits on the steel mating surface. The formation of the carbonaceous layer is associated with high wear and is the result of the chemical reaction between MoDTC and a-C:H coating.

A positive effect is obtained with BO +MoDTC in ta-C systems, resulting in a very low coefficient of friction and little to no wear in the coating. For the first time, a distinct MoS_2 -containing tribo layer is demonstrated on a DLC coating, leading to a very low coefficient of friction (below 0.04).

In a similar study, Hofmann and Co. reported experimental investigations on friction and contact temperature of an amorphous, hydrogenated and metal-containing a-C:H: Zr DLC coating (ZrCg) and a MoS₂-bonded coating (BoC). Accordingly, the ZrCg DLC coating is more favorable in friction than the MoS₂ BoC. Nevertheless, the friction coefficients are higher compared to oil lubricated contacts. Contact temperature measurements using thin film sensors show thermal isolation for MoS₂-BoC due to its low thermal diffusivity. Since MoS₂ is sensitive to oxygen, high contact temperatures can promote oxidation processes, e.g., from MoS_2 to MoO_3 . This can lead to a structural change, resulting in high friction and system failure. In another similar study, Hofmann and Co. are investigating the friction and temperature behavior of surface coatings in rolling-sliding contacts for use in dry-lubricated gears. For this work, uncoated polished surfaces were tested under dry and oilinjection lubrication. In an experimental setup on a two-disk test rig, case-hardened 16MnCr5E (AISI5115) steel is considered as the substrate material, as well as an amorphous, hydrogenated and metal-containing a-C:H:Zr DLC coating (ZrCg) and a MoS₂-bonded coating (MoS₂-BoC). The results of contact temperature measurements show a pronounced thermal insulation with MoS_2 -BoC, which can disrupt the sliding mechanism of MoS_2 by accelerated oxidation. The study shows that the application of dry lubricated gears under ambient air conditions is challenging because the tribological and thermal behavior requires tailored surface coatings [61].

Masuko and et. investigated the wear behavior of the three DLCs (H-DLC and NH-DLC or ta-DLC) and steel specimens lubricated with MoDTC, ZnDTP and MoDTC+ZnDTP. Accordingly, it was found that the formulation with the ZnDTP additive reduced the wear of all specimens regardless of the presence of MoDTC. In the case of the single formulated MoDTC, both the ta-C and steel samples showed wear reduction, but both hydrogenated DLCs showed increased wear, especially the high hydrogen DLC (a C:30H) [62].

In general, one or a combination of the following mechanisms can be expected for the DLC wear process: (1) MoDTC-derived MoO_3 or iron oxide particles from the ferrous counterpart promote the abrasive wear of the DLC coating, (2) molyloxides (molybdates) formed under tribological conditions act as a catalyst for the oxidation or/and dehydrogenation of the DLC coating [63].

The effect of molybdenum dithiocarbamate (MoDTC) additives on the lubrication performance of carbonbased coatings has been the subject of much research, which shows that a high wear rate occurs when the MoDTC is added to the base oil. Molybdenum carbide is widely used for cutting tools and abrasives due to its high hardness. For this reason, the mechanical properties of the MoC-containing tribofilm formed on the steel ball were investigated using nanoindentation to determine whether abrasive wear should be considered during the observed wear process [64].

In the other study, De Feo and *et al.* compared two DLCs (a-C:H DLC and the silicon and oxygen doped DLC). It is believed that this will lead to a better understanding of the DLC wear mechanisms in the presence of MoDTC additives. Accordingly, the silicon and oxygen doped DLC coating (Si-doped DLC) is the only one that exhibits relatively high friction associated with dramatic wear. All tribological experiments and analytical results of this work support the assumption that the formation of a molybdenum carbide compound is an important step in the mechanism determining the wear of DLC coatings.

Ref	Type of DLC	Deposition technique	Interlayer	Additives	Lubricants	Friction (COF)
Kashyap	DLC	electro	Mo	Si	-	0.11
Ueda	DLC	Physical vapor	MoO ₃	ZDDP,	PAO+Mo	0.9-0.11
Banerji	DLC	electro	MoS_2	Ti	-	0.05-0.12
Taib	DLC	-	MoDTC	TiC,TiN.SUJ2	ZnDTP	0.08-0.14
Müller	DLC	electro	Mo-W	-	Al_2O_3	0.15-0.25

Table 1. Summary of studies on solid lubricants in the presence of various additives.

sliding against a steel counterpart in the presence of MoDTC additives. The formation of this carbide compound was demonstrated for the first time on the surface of the steel counterpart. They proposed a new wear scenario consisting of different steps:

During the initial running-in phase, the MoDTC additive reacts preferentially with the steel surface and forms a MoS_{2} - and/or $MoS_{2x}O_x$ -based tribofilm on the steel, compounds that can lower the coefficient of friction. During further sliding, this molybdenumbased tribofilm interacts with the dangling carbon bonds of the Si doped DLC surface formed by breaking the Si-C bond network. The reaction between the molybdenum in the tribofilm formed on the steel counterpart and the carbon of the DLC coating leads to the formation of molybdenum carbide (Mo_xC), resulting in an increase in friction and wear rate, as shown by the surface analyses [65].

The wear resistance of MoS₂ in lubrication applications can be enhanced by doping MoS2 with composites. Banerji and et al. [66] investigated a Ti doped multilayer MoS₂ coating (Ti-MoS₂) intended for use in engineering applications at elevated temperatures such as hot working or machining of light Al alloys. In tests conducted between 25 °C and 200 °C, the COF decreased progressively from 0.11 to a minimum value of 0.05. The higher COF at 25 °C compared to that at 200 °C was due to the presence of moisture (45% RH) in the environment. The increase in COF of MoS₂ in a humid environment was attributed to either oxidation to MoO₃ or water adsorption on MoS₂ layers. However, the addition of Ti to the MoS₂ coatings resulted in a relatively low steady-state COF of 0.11 at 45% RH compared to the reported COF values of 0.14 and 0.15 for monolithic MoS2 coatings tested against steel at room temperature ambient conditions. The improved frictional behaviour was attributed to the presence of Ti atoms in interstitial spaces between the S planes, which prevent the adsorption of water molecules. As temperature increased, moisture was removed and COF values decreased to 0.05 at 200 $^\circ\text{C}.$

5. Tribological Behaviour of Machine Elements Having DLC and Lubricated with MoDTC

Much research is concerned with the effects of MoDTC additives on the lubrication performance of carbon-based coatings. In the same direction, Feo et al. [67] analyzed the friction and wear behavior of an amorphous hydrogenated DLC coating doped with silicon and oxygen when lubricated by oils containing MoDTC. They showed that a high wear rate occurs when the MoDTC is mixed with the base oil. They also analyzed the performance of a-C:H and a-C:h:Si:O and found that MoDTC-containing base oil has less effect on the DLC/steel contact than on the steel/steel contact. Another experiment addressed the effect of oil with ZDDP or without ZDDP on lubricant behavior. Kosarieh et al.[63] found that the wear behavior of the hydrogenated DLC coating depended not only on the presence of ZDDP in the oil formulation but also on the nature of the counterpart. This study found that the steel counterpart is a critical component of the tribocouple that leads to the MoDTC-induced wear of the hydrogenated DLC. Since temperature is an important parameter in the analysis of lubricants, Kashyap et al.[68] decided to analyze the behavior of the DLC coating in combination with Mo-DTC at 300 degrees room temperature. They found that a multilayer coating of molybdenum, Mo, and DLC was deposited by dual sputtering using a high-power pulsed magnetron sputtering current source (HiPIMS) for the graphite target and a pulsed current source for the Mo [68], [69], [66], [70], [71] target. The MoDLC multilayer coating was optimized for wear protection and low friction. The coated sample failed at 15 MPa, while the uncoated samples failed at 5 MPa. Also, when the specimens were tested at 300 °C, they showed similar results. To investigate the effects of humid air on solid lubricants, some researchers have looked at H-DLC in

humid air. In the same direction, Yu et al. [72] aimed to achieve superlubricity in humid air. They worked on H-DLC and its multilayer films with MoS₂ and DLC. Thus, they found that the COF is 0.004±0.001 on average. The result is that we can reduce the friction of DLC and H-DLC by adding MoDTC to the films. Through this research, we found that temperature, air conditioning, the addition of a lubricant such as oil, and the properties of the oil are the most effective parameters to reduce friction in DLC and H-DLC coatings. Constantinou 2017 et al. [73] and Haji Ghasemi et al [74] experimented with new methods to deposit Mo on DLC surface. Their aim was to use pulsed laser deposition and plasma nitriding, respectively. As a result, Constantinou 2017 et al found that COF could be reduced to 0.12%-0.14% and Ghasemi to 50% by depositing a DLC coating on various nitrided samples, which can be attributed to the high wear resistance of DLC coatings.

Drilling of aluminum alloys in the absence of cooling lubricants is challenging. Assurin Hassan *et al.* [75] therefore decided to use MoS_2 and DLC to improve the drilling prosecco. The results showed that these coated drills allowed less aluminum pickup on the drills and minimized the variation in diameter deviation and surface roughness of the hole. The work demonstrates that dry drilling of stacked aluminum alloys is possible, eliminating the health and safety risk associated with the use of oil in mobile drill heads.

Table 1 is a summary of research in the field of solid lubricants in the presence of various additives. In this research, various deposition techniques have been tested and each has its own unique results. As the table shows, DLC with MoS_2 in the presence of the additive Ti has the lowest coefficient of friction and with Mow without any additive has almost the highest coefficient of friction.

6. Conclusion and outlook

Solid lubricants can still be used in applications for which oils and greases are not suitable or cannot be considered. State-of-the-art deposition technologies make it possible to significantly change the properties and structure of MoS_2 through co-deposition, multiple coating, and the fabrication of composite layers. Periodic nanolayers can improve fracture toughness. On this basis, it is possible to optimize the thickness of metal and MoS_2 layers. Ti has been used by several researchers due to its adhesion promoting properties and compatibility with multilayers. In humid air, the mechanism of failure of MoS₂, can be summarized as oxidation to MoO₃, followed by bubbling and breakup of the film exposing the steel substrate, leaving a powdered mixture of molybdenum and iron oxides. In dry atmosphere or vacuum, failure is generally due to gradual depletion of MoS2 by lateral flow. Recent activity has produced improvements in coating technologies, an understanding of wear mechanisms and the complex friction of MoS, and the possibilities available to materials engineering to combine it with other materials and in other forms.

7. References

- G. Dearnaley, J.H. Arps, Biomedical applications of diamond-like carbon (DLC) coatings: A review, Surface and Coatings Technology, 2518-2524, 200 (2005).
- 2. R. Hauert, A review of modified DLC coatings for biological applications, Diamond and related materials, 583-589, 12 (2003).
- A. Erdemir, J.M. Martin, Superior wear resistance of diamond and DLC coatings, Current Opinion in Solid State and Materials Science, 243-254, 22 (2018).
- 4. X. Wu, M. Suzuki, T. Ohana, A. Tanaka, Characteristics and tribological properties in water of Si-DLC coatings, Diamond and related materials, 7-12, 17 (2008).
- L. Čoga, S. Akbari, J. Kovač, M. Kalin, Differences in nano-topography and tribochemistry of ZDDP tribofilms from variations in contact configuration with steel and DLC surfaces, Friction, 296-315, 10 (2022).
- 6. J. Vetter, 60 years of DLC coatings: historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications, Surface and Coatings Technology, 213-240, 257 (2014).
- 7. D.K. Rajak, A. Kumar, A. Behera, P.L. Menezes, Diamond-like carbon (DLC) coatings: Classification, properties, and applications, Applied Sciences, 4445, 11 (2021).
- 8. B. Vengudusamy, J.H. Green, G.D. Lamb, H.A. Spikes, Tribological properties of tribofilms formed from ZDDP in DLC/DLC and DLC/steel contacts, Tribology International, 165-174, 44 (2011).
- 9. S. Grigoriev, M. Volosova, S. Fyodorov, M. Lyakhovetskiy, A. Seleznev, DLC-coating application to improve the durability of ceramic

tools, Journal of Materials Engineering and Performance, 4415-4426, 28 (2019).

- F. Sanchette, M. El Garah, S. Achache, F. Schuster, C. Chouquet, C. Ducros, A. Billard, DLC-based coatings obtained by low-frequency plasmaenhanced chemical vapor deposition (LFPECVD) in cyclohexane, principle and examples, Coatings, 1225, 11 (2021).
- M. Kalin, E. Oblak, S. Akbari, Evolution of the nano-scale mechanical properties of tribofilms formed from low-and high-SAPS oils and ZDDP on DLC coatings and steel, Tribology International, 43-56, 96 (2016).
- 12. R. Zahid, M.B.H. Hassan, M. Varman, R.A. Mufti, M.A. Kalam, N.W.B.M. Zulkifli, M. Gulzar, A review on effects of lubricant formulations on tribological performance and boundary lubrication mechanisms of non-doped DLC/DLC contacts, Critical Reviews in Solid State and Materials Sciences, 267-294, 42 (2017).
- 13. A. Zeng, V.F. Neto, J.J. Gracio, Q.H. Fan, Diamond-like carbon (DLC) films as electrochemical electrodes, Diamond and Related Materials, 12-22, 43 (2014).
- 14. P. Manimunda, A. Al-Azizi, S.H. Kim, R.R. Chromik, Shear-induced structural changes and origin of ultralow friction of hydrogenated diamondlike carbon (DLC) in dry environment, ACS applied materials & interfaces, 16704-16714, 9 (2017).
- 15. R. Hauert, An overview on the tribological behavior of diamond-like carbon in technical and medical applications, Tribology International, 991-1003, 37 (2004).
- 16. K. Weicheng, Y. Zhou, H. Jun, Electrochemical performance and corrosion mechanism of Cr–DLC coating on nitrided Ti6Al4V alloy by magnetron sputtering, Diamond and Related Materials, 108398, 116 (2021).
- 17. J.D. Schall, G. Gao, J.A. Harrison, Effects of adhesion and transfer film formation on the tribology of self-mated DLC contacts, The Journal of Physical Chemistry C, 5321-5330, 114 (2010).
- D. Martinez-Martinez, J.T.M. De Hosson, On the deposition and properties of DLC protective coatings on elastomers: A critical review, Surface and Coatings Technology, 677-690, 258 (2014).
- Y. Zhou, L. Li, W. Shao, Z. Chen, S. Wang, X. Xing, Q. Yang, Mechanical and tribological behaviors of Ti-DLC films deposited on 304 stainless steel: Exploration with Ti doping from micro to macro, Diamond and Related Materials, 107870, 107 (2020).
- 20. B. Vengudusamy, J.H. Green, G.D. Lamb, H.A. Spikes, Behaviour of MoDTC in DLC/DLC and

DLC/steel contacts, Tribology International, 68-76, 54 (2012).

- L.V. Santos, V.J. Trava-Airoldi, K. Iha, E.J. Corat, M.C. Salvadori, Diamond-like-carbon and molybdenum disulfide nanotribology studies using atomic force measurements, Diamond and related materials, 1049-1052, 10 (2001).
- 22. I. Sugimoto, F. Honda, K. Inoue, Analysis of wear behavior and graphitization of hydrogenated DLC under boundary lubricant with MoDTC, Wear, 124-128, 305 (2013).
- 23. T. Shinyoshi, Y. Fuwa, Y. Ozaki, Wear analysis of DLC coating in oil containing Mo-DTC, SAE Technical Paper. 2007.
- T. Haque, A. Morina, A. Neville, Influence of friction modifier and antiwear additives on the tribological performance of a non-hydrogenated DLC coating, Surface and Coatings Technology, 4001-4011, 204 (2010).
- 25. T. Haque, A. Morina, A. Neville, Effect of friction modifiers and antiwear additives on the tribological performance of a hydrogenated DLC coating, (2010).
- I. Sugimoto, Mechanism on specific wear of DLC film in engine oil with Mo-DTC, Trans. Jpn. Soc. Mech. Eng. Ser. A, 213-222, 78 (2012).
- M.A.A. Shahmirzadi, A. Kargari, Nanocomposite membranes, Emerging technologies for sustainable desalination handbook, Elsevier2018, pp. 285-330.
- D.D. Kumar, P. Kuppusami, G.S. Kaliaraj, S.S. Sana, A.K.J.T. Kirubaharan, C.o.S. Coatings, Tribological Properties of Carbon-Based Coatings, 115-137, (2022).
- 29. S. Ahmed, V.S. Dakre, Tribology and Characterization of Surface Coatings, John Wiley & Sons2022.
- A. Tyagi, R. Walia, Q. Murtaza, S.M. Pandey, P.K. Tyagi, B.J.I.j.o.r.m. Bajaj, h. materials, A critical review of diamond like carbon coating for wear resistance applications, 107-122, 78 (2019).
- 31. C. Li, Thermal spraying of light alloys, Surface engineering of light alloys, Elsevier2010, pp. 184-241.
- 32. P.L. Fauchais, J.V. Heberlein, M.I. Boulos, Overview of thermal spray, Thermal spray fundamentals, Springer2014, pp. 17-72.
- F. Nasirpouri, K. Alipour, F. Daneshvar, M.-R. Sanaeian, Electrodeposition of anticorrosion nanocoatings, Corrosion Protection at the Nanoscale, Elsevier2020, pp. 473-497.
- B. Moore, E. Asadi, G.J.A.i.M.S. Lewis, Engineering, Deposition methods for microstructured and nanostructured coatings on metallic bone implants: a review, 2017 (2016).

- M. Hong, J. Zou, Z.-G. Chen, Synthesis of thermoelectric materials, Thermoelectricity and Advanced Thermoelectric Materials, Elsevier2021, pp. 73-103.
- 36. M.F. Montemor, Smart composite coatings and membranes: Transport, structural, environmental and energy applications, Elsevier2015.
- 37. R. Zahid, H.H. Masjuki, M. Varman, M.A. Kalam, R.A. Mufti, N.W.B.M. Zulkifli, M. Gulzar, S.S.B.N.J.J.o.M.R. Azman, Influence of intrinsic and extrinsic conditions on the tribological characteristics of diamond-like carbon coatings: A review, 1814-1836, 31 (2016).
- M.M. Al-Asadi, H.A.J.T.I. Al-Tameemi, A review of tribological properties and deposition methods for selected hard protective coatings, 107919, (2022).
- P. Yi, D. Zhang, D. Qiu, L. Peng, X.J.I.J.o.H.E. Lai, Carbon-based coatings for metallic bipolar plates used in proton exchange membrane fuel cells, 6813-6843, 44 (2019).
- F.M. Borodich, E. Brousseau, A. Clarke, A. Pepelyshev, J.C.J.F.i.M.E. Sánchez-López, Roughness of deposited carbon-based coatings and its statistical characteristics at nano and microscales, 24, 5 (2019).
- 41. J.J.S. Vetter, C. Technology, 60 years of DLC coatings: historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications, 213-240, 257 (2014).
- 42. X. Deng, H. Kousaka, T. Tokoroyama, N.J.T.i. Umehara, Tribological behavior of tetrahedral amorphous carbon (ta-C) coatings at elevated temperatures, 98-103, 75 (2014).
- 43. T. Kasiorowski, J. Lin, P. Soares, C. Lepienski, C. Neitzke, G. De Souza, R.J.S. Torres, C. Technology, Microstructural and tribological characterization of DLC coatings deposited by plasma enhanced techniques on steel substrates, 125615, 389 (2020).
- 44. C. Matta, M. De Barros Bouchet, T. Le-Mogne, B. Vachet, J. Martin, T.J.L.S. Sagawa, Tribochemistry of tetrahedral hydrogen-free amorphous carbon coatings in the presence of OH-containing lubricants, 137-149, 20 (2008).
- 45. D.D. Kumar, P. Kuppusami, G.S. Kaliaraj, S.S. Sana, A.K. Kirubaharan, Tribological Properties of Carbon-Based Coatings, Tribology and Characterization of Surface Coatings, 115-137, (2022).
- K. Bewilogua, D. Hofmann, History of diamondlike carbon films—From first experiments to worldwide applications, Surface and Coatings Technology, 214-225, 242 (2014).
- 47. X. Li, D. Zhang, K.-R. Lee, A. Wang, Effect of metal doping on structural characteristics of

amorphous carbon system: A first-principles study, Thin Solid Films, 67-72, 607 (2016).

- 48. P. Yi, D. Zhang, D. Qiu, L. Peng, X. Lai, Carbonbased coatings for metallic bipolar plates used in proton exchange membrane fuel cells, International Journal of Hydrogen Energy, 6813-6843, 44 (2019).
- 49. M. Grischke, K. Bewilogua, K. Trojan, H. Dimigen, Application-oriented modifications of deposition processes for diamond-like-carbon-based coatings, Surface and Coatings Technology, 739-745, 74 (1995).
- 50. X. Sun, J. Zhang, W. Pan, W. Wang, C.J.J.o.A. Tang, Compounds, Research progress in surface strengthening technology of carbide-based coating, 164062, (2022).
- 51. D.D. Kumar, N. Kumar, S. Kalaiselvam, R. Radhika, A.M. Rabel, R.J.T.I. Jayavel, Tribomechanical properties of reactive magnetron sputtered transition metal carbide coatings, 234-244, 114 (2017).
- 52. U. Jansson, E.J.T.S.F. Lewin, Sputter deposition of transition-metal carbide films—A critical review from a chemical perspective, 1-24, 536 (2013).
- D. Nilsson, F. Svahn, U. Wiklund, S.J.W. Hogmark, Low-friction carbon-rich carbide coatings deposited by co-sputtering, 1084-1091, 254 (2003).
- A.R. Govande, A. Chandak, B.R. Sunil, R.J.I.J.o.R.M. Dumpala, H. Materials, Carbidebased thermal spray coatings: A review on performance characteristics and post-treatment, 105772, (2021).
- 55. J.-F. Yang, Y. Jiang, J. Hardell, B. Prakash, Q.-F. Fang, Influence of service temperature on tribological characteristics of self-lubricant coatings: A review, Frontiers of Materials Science, 28-39, 7 (2013).
- 56. J. Kogovšek, M. Remškar, M. Kalin, Lubrication of DLC-coated surfaces with MoS2 nanotubes in all lubrication regimes: Surface roughness and runningin effects, Wear, 361-370, 303 (2013).
- 57. I. Singer, S. Dvorak, K. Wahl, T. Scharf, Role of third bodies in friction and wear of protective coatings, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, S232-S240, 21 (2003).
- C. Baker, J. Hu, A. Voevodin, Preparation of Al2O3/DLC/Au/MoS2 chameleon coatings for space and ambient environments, Surface and Coatings Technology, 4224-4229, 201 (2006).
- 59. D.-Y. Wang, C.-L. Chang, W.-Y. Ho, Microstructure analysis of MoS2 deposited on diamond-like carbon films for wear improvement, Surface and Coatings Technology, 123-127, 111 (1999).

- C. Espejo, B. Thiébaut, F. Jarnias, C. Wang, A. Neville, A. Morina, MoDTC tribochemistry in steel/steel and steel/diamond-like-carbon systems lubricated with model lubricants and fully formulated engine oils, Journal of Tribology, 012301, 141 (2019).
- S. Hofmann, M. Yilmaz, E. Maier, T. Lohner, K. Stahl, Friction and contact temperature in dry rolling-sliding contacts with MoS2-bonded and aC: H: Zr DLC coatings, International Journal of Mechanical and Materials Engineering, 1-12, 16 (2021).
- 62. M. Masuko, T. Ono, S. Aoki, A. Suzuki, H. Ito, Friction and wear characteristics of DLC coatings with different hydrogen content lubricated with several Mo-containing compounds and their related compounds, Tribology International, 350-357, 82 (2015).
- 63. S. Kosarieh, A. Morina, J. Flemming, E. Lainé, A. Neville, Wear mechanisms of hydrogenated DLC in oils containing MoDTC, Tribology Letters, 1-17, 64 (2016).
- D. Jianxin, S. Wenlong, Z. Hui, Z. Jinlong, Performance of PVD MoS2/Zr-coated carbide in cutting processes, International Journal of Machine Tools and Manufacture, 1546-1552, 48 (2008).
- 65. M. De Feo, M.D.B. Bouchet, C. Minfray, T. Le Mogne, F. Meunier, L. Yang, B. Thiebaut, J. Martin, MoDTC lubrication of DLC-involving contacts. Impact of MoDTC degradation, Wear, 116-125, 348 (2016).
- A. Banerji, S. Bhowmick, A. Alpas, Role of temperature on tribological behaviour of Ti containing MoS2 coating against aluminum alloys, Surface and Coatings Technology, 2-12, 314 (2017).
- 67. M. De Feo, M.D.B. Bouchet, C. Minfray, C. Esnouf, T. Le Mogne, F. Meunier, L. Yang, B. Thiebaut, S. Pavan, J. Martin, Formation of interfacial molybdenum carbide for DLC lubricated by

MoDTC: Origin of wear mechanism, Wear, 17-28, 370 (2017).

- 68. A. Kashyap, A. Harsha, P. Kondaiah, H.C. Barshilia, Study on galling behaviour of HiPIMS deposited Mo/DLC multilayer coatings at ambient and elevated temperature, Wear, 204327, 498 (2022).
- 69. M. Ueda, A. Kadiric, H. Spikes, Wear of hydrogenated DLC in MoDTC-containing oils, Wear, 203869, 474 (2021).
- 70. M.T. bin Taib, N. Umehara, T. Tokoroyama, M. Murashima, D. Tunggal, The effects of oil additives and mating materials to the friction, wear and seizure characteristics of aC: H coating, Jurnal Tribologi, 1-19, 18 (2018).
- I.C. Müller, J. Sharp, W.M. Rainforth, P. Hovsepian, A. Ehiasarian, Tribological response and characterization of Mo–W doped DLC coating, Wear, 1622-1629, 376 (2017).
- 72. G. Yu, Z. Gong, B. Jiang, D. Wang, C. Bai, J. Zhang, Superlubricity for hydrogenated diamond like carbon induced by thin MoS2 and DLC layer in moist air, Diamond and Related Materials, 107668, 102 (2020).
- 73. M. Constantinou, M. Pervolaraki, L. Koutsokeras, C. Prouskas, P. Patsalas, P. Kelires, J. Giapintzakis, G. Constantinides, Enhancing the nanoscratch resistance of pulsed laser deposited DLC films through molybdenum-doping, Surface and Coatings Technology, 185-195, 330 (2017).
- 74. M.H. Ghasemi, B. Ghasemi, H.R.M. Semnani, Wear performance of DLC coating on plasma nitrided Astaloy Mo, Diamond and Related Materials, 8-15, 93 (2019).
- 75. S.R.A. Hassan, P.T. Mativenga, K. Cooke, H. Sun, S. Field, M. Walker, J. Chodynicki, C. Sharples, B. Jensen, M.F. Mortensgaard, Lubricant Coatings for Mobile Dry Drilling of Stacked Aluminium Alloys, (2021).