Environmental and Thermal Effects on the Tribological Performance of DLC Coatings

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Abstract Diamond-like carbon (DLC) coatings have low friction and high wear resistance compared to bulk materials and to other wear-resistant coated surfaces. The surrounding environment, gas atmosphere, humidity and temperature, affect the friction and wear performance of DLC films dramatically. In dry and inert atmospheres, the highly hydrogenated DLC films typically exhibit low friction performance, but the hydrogen-free DLC films have high friction accompanied with increased wear. In humid environment, the friction coefficient of both types of DLC films is similar varying in the range 0.05–0.2 and the best wear resistance can be achieved with hydrogen-free ta-C films. At elevated temperatures, the advantageous tribological properties of hydrogenated DLC films may be disturbed due to effusion of hydrogen and graphitization of the film structure in rather low temperatures. The hydrogen-free ta-C films on the other hand can survive in higher temperatures, even though the friction coefficient reaches higher values.

Keywords diamond-like carbon, DLC, hydrogenated, hydrogen-free, environment, humidity, temperature

1 Introduction

Diamond-like carbon (DLC) coatings have attracted great interest during the past decades due to their excellent mechanical, electrical and chemical properties. DLC is a metastable form of amorphous carbon with exceptional properties, like high hardness and chemical inertness providing favourable friction and wear properties.

DLC films cover a wide range of different types of coatings with similar, yet differing tribological properties. The two major categories of DLCs are the hydrogenated and hydrogen-free DLC films. The hydrogenated DLC films typically have hydrogen content from 20 to 40 at. % and the hydrogen-free DLC films have

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only a small fraction of hydrogen as an impurity in the film structure. The composition of DLC films has been described in a ternary phase diagram of hydrogen content, sp^3 and sp^2 hybridization [112]. Using this classification, the major groups of DLC films that have been investigated mostly are hydrogenated amorphous carbon (a-C:H), amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C). A great interest has been addressed particularly to the tribological performance of a-C:H films deposited mostly with plasma-assisted chemical vapour deposition (PACVD) processes. Studies on the hydrogen-free a-C films, deposited with sputtering processes, and the hydrogen-free ta-C coatings, deposited by vacuum arc or laser ablation processes, have also been carried out, but to a lesser extent. The friction and wear performance of DLC films is greatly influenced by the intrinsic coating properties, the functional parameters applied and the environmental conditions. The environmental aspects affecting the tribological performance of DLC films will be reviewed in this chapter in respect of gas atmosphere, humidity and temperature.

2 Tribological Performance of DLC Coatings

The DLC coatings can be considered as low-friction coatings with high wear resistance compared to most bulk materials: for example, wear-resistant ceramic coatings, such as TiN. The TiN typically has a friction coefficient of about 0.5 against a steel counterpart, whereas DLC films exhibit friction coefficient less than 0.2 in normal atmosphere. In unlubricated contacts, the DLC coatings typically show similar friction values compared to boundary-lubricated steel against steel contacts. The wear resistance of DLC coatings also outperforms most wear-resistant materials and coatings in sliding contacts, since the wear rates of DLC films are two to three orders of magnitude lower compared to, e.g. TiN coating [115–117,120,139].

The DLC films cover a great variety of compositions and structures controlled by the deposition technique and deposition parameters. The film composition together with the test conditions (load and speed), test environment, temperature and counterface material influence the friction and wear performance of DLC films as reviewed in several publications [21,22,37,42,53,54]. Table 1 represents the typical friction and wear rate data of different types of DLC films.

3 Environmental Effects on Tribological Performance of DLC Films

The test environment has a dramatic influence on the friction and wear performance of hydrogenated and hydrogen-free DLC films. In dry air and in inert gasses the friction of hydrogenated DLC films is low, reaching superlow values in the range 0.001–0.02, when the films are highly hydrogenated. In humid air, the friction

Table 1 Friction coefficients values and wear rates from the literature for diamond, diamond-like carbon and doped DLC coatings

	Diamond coatings	Hydrogen free DLC	Hydrogenated DLC	Modified/ doped DLC	References used
Structure	CVD diamond	a-C ta-C	a-C:H ta-C:H	a-C:Me a-C:H:Me a-C:H:x Me=W,Ti…. x=Si,O,N, F,B...	[3,4,11,20,31,33,34, 37,42,45,48,51, 60,64,68,98,107, 118,119,122, 128,131,136,150]
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)	

K refers to wear rate [$x10^{-6}mm^3(Nm)^{-1}$]

coefficient of hydrogenated DLC films increases to values 0.1–0.2. Similar values of friction coefficient are typically measured for the hydrogen-free DLC films in humid environment. However, the hydrogen-free DLC films have a high friction in dry conditions. The friction performance of hydrogenated and hydrogen-free DLC films is schematically represented in Fig. 1 indicating the high, low and superlow regimes of friction performance.

The superlow friction performance of hydrogenated DLC films in dry and inert environments has been attributed to the hydrogen-terminated dangling bonds with weak van der Waals forces acting in the contact between surfaces. In the humid oxygen-containing environment, this mechanism will be disturbed by water vapour molecules causing a tenfold increase in friction. Another mechanism affecting the tribological performance of the DLC films is the

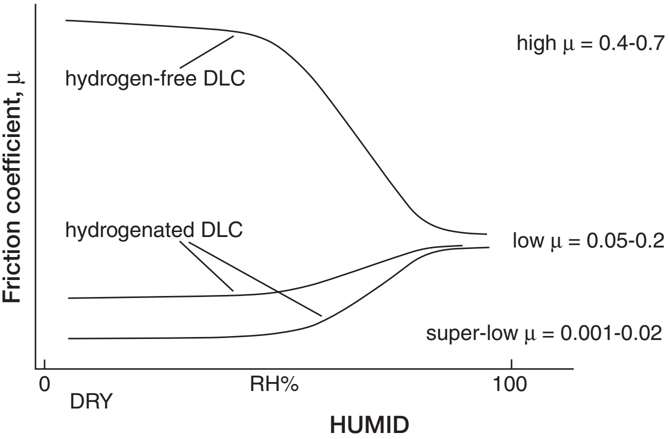

Fig. 1 The effect of humidity on the friction performance of hydrogenated and hydrogen-free DLC films as the relative humidity of the environment is increased

graphitization, which occurs on the contact surface of DLC films under tribological action. In the micrographitization process, the mechanical interactions between the sliding interfaces lead to graphitization at the micro-contact regions. In different atmospheres also material transfer will occur and the formation of transfer layer is evident, as reported by several authors. These layers have been shown to influence both the friction and wear performance of DLC films and counterparts.

The wear rates of DLC films are typically in the range 10^{-6} to 10^{-10} mm^3 $(Nm)^{-1}$ (see Table 1) and the wear resistance varies according to the structural features of the DLC films. Moreover, the environment can influence the wear behaviour, since a correlation has been found for the friction and wear performance of the DLC films. In general, the high friction is accompanied by high wear, as reported for the hydrogen-free films in an inert gas or in vacuum. Close correlation has also been shown between the friction and wear coefficients of hydrogenated DLC films in dry nitrogen, since the wear rates decrease with the decreasing friction coefficient as shown in Fig. 2 [22].

3.1 The Friction and Wear Performance of Hydrogenated DLC Films in Vacuum and Inert Environments

Hydrogenated DLC films have low friction coefficient in vacuum and in inert environments. Already in the pioneering work of Enke et al. [18], friction coefficient values of 0.005–0.02 were measured when the hydrogenated DLC

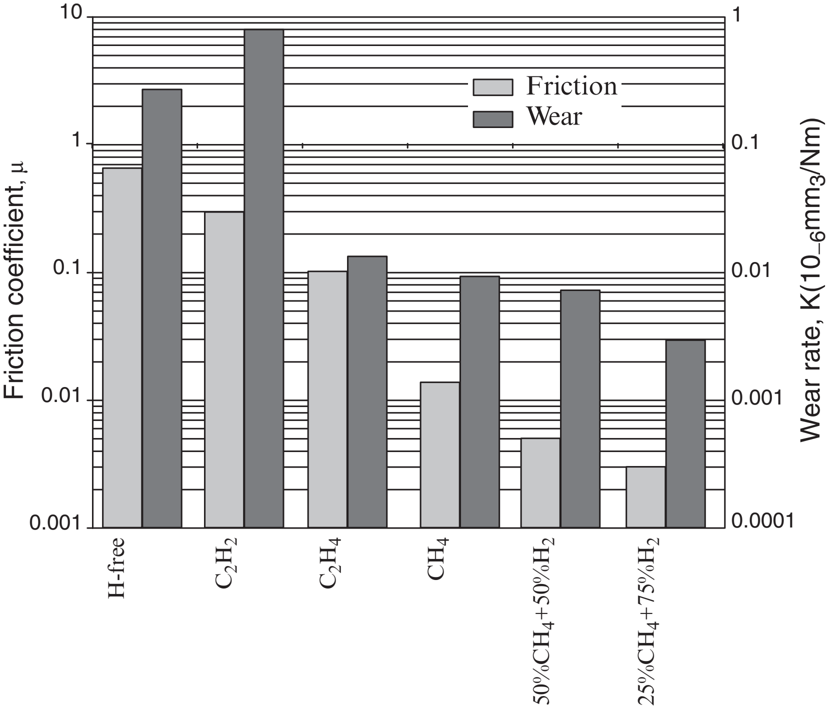

Fig. 2 The friction coefficients and wear rates of DLC films derived from different carbon sources and containing various hydrogen to carbon ratios. The tests were carried out in dry nitrogen. (After [22].)

films were sliding against steel in vacuum conditions ($p_{H_2O} = 10^{-8}$ Torr). As the partial pressure of water vapour increased (10^{-1} Torr), the friction increased to 0.19. A similar performance was also observed in nitrogen atmosphere as the relative humidity was increased [17,18]. Memming et al. [89] also measured friction values down to 0.02 in ultra-high vacuum (UHV), in dry nitrogen and in low humidity (<1% RH) conditions. However, in humid nitrogen and oxygen the friction coefficient values were about 0.25 and increased in dry oxygen up to 0.6. Similar observations have also been made by several other authors [13,24,61,98,108]. Examples of typical friction and wear rate values reported for hydrogenated DLC (a-C:H) films are represented in Table 2.

3.1.1 Hydrogenated DLC Films with Superlow Friction Performance in Inert Environment

The low friction performance of hydrogenated DLC films has been shown to reach superlow values in inert and dry environments. Donnet et al. [13] measured the friction coefficient values in the range 0.006–0.008 for steel balls sliding against

Table 2 The friction coefficient values and wear rates of the hydrogenated DLC coatings tested in different environments

DLC film		Tribological testing						
Film (substrate)	Deposition technique	Counter material	Load [N]/[GPa]	Speed [ms^{-1}]	Environment	Friction Coefficient	Wear rate [x10^{-6} mm^3(Nm)$^{-1}$]	Reference Author year
a-C:H (Si)	PACVD	Steel	1 N	(1000 rpm)	Vacuum (p_{H2O}= 1.3x10^{-6} Pa)	0.005–0.02	–	[17,18]
					RH 100 %			
						0.19	–	
a-C:H (Si)	PACVD	Steel	0.8 N		UHV	0.02	–	[89]
					Dry N_2	0.02	–	
					Humid N_2	0.25	–	
					Dry O_2	0.6	–	
a-C:H (Si3N4)	PACVD	Si_3N_4	1–1.7 N/	50–	Air	0.2–0.3	–	[97]
			0.91 GPa	133·10^{-6}	Nitrogen	0.01–0.15	–	[98]
					Vacuum +high temp	0.1–1.3	–	
a-C:H (SiC)	IB	Si_3N_4	1–20 N /	0.026	Ar	0.04	0.00046	[24]
			0.4–1.5 GPa		N_2	0.03	0.0009	
					Dry air	0.07	0.0192	
					Ambient air	0.15	0.0724	
a-C:H (steel)	d.c.CVD	Steel	2 N	0.03-0.09	Vacuum 10-6 Pa	0.08	–	[108]
a-C:H (Si)	PACVD	Stainless steel	4 N/	0.0017	10^{-7}–10^{-1} Pa	0.006–0.008	–	[13]
			1 GPa		10 Pa–50 Pa	0.01–0.07	–	
					10^5 Pa (RH 40 %)	0.15	–	
					Dry N_2 (RH<2%)	0.02	–	

a-C:H (AISI 440B)	PACVD	Al_2O_3	5–40 N	0.1–3.0	Ambient air (50 % RH)	0.02–0.13	0.046–0.16	[118]
a-C:H	PACVD	AISI 52100	3.3-20 N/ 0.8–1.45 GPa	1-500 rpm	Vacuum (2x10^{-4} Pa) Dry N_2 Amb. air (RH 50 %)	0.003–0.009 0.006–0.015 0.10–0.23	2.2–7.8 0.026–0.091 0.098–0.194	[134]
a-C:H (steel)	PACVD	a-C:H (AISI M50)	10 N/ 1.04 GPa	0.5	Dry N_2	0.003–0.0005	0.00046–0.00015	[30]
a-C:H/ diff. at.% H (Si)	PACVD	Steel	1 GPa	0.0012	Vacuum (<10^{-7} Pa) Ambient air (25-40 %RH)	0.004–0.068 -	- 0.018–0.11	[123]
a-C:H (Si)	PACVD	SiC	1 N	0.1	Vacuum N2 O2 Dry air (RH 4-6 %)	0.17 0.06 0.1 0.07	0.0017 0.0022 0.515 0.113	[149]
a-C:H (Si)	PACVD	AISI 440C	1.06–3.08 N/ 1.2–1.8 GPa	0.0042-0.025	High humidity (RH 90–95 %) Low humidity (RH 17–20 %)	0.12–0.17 0.05–0.22	0.016–0.022 0.022–0.025	[150]
a-C:H (Si)	PACVD	AISI 440C	10 N/ 1.6 GPa	0.02	Ambient air (RH 25–45 %)	0.03–0.1	0.02–0.1	[127]
a-C:H (AISI 440C)	PACVD	AISI 440C	9.4 N	0.016	Ambient air (RH 40–60 %)	0.15–0.25	0.19–0.057	[104]
a-C:H (AISI 440C)	ECR–CVD	AISI 52100	1–10 N/ 0.7–1.5 GPa	0.02–0.15	Ambient air (RH 45–55 %)	0.18–0.22	0.03–0.08	[75,76]
a-C:H (Si)	PACVD	AISI 52100	2 N	2	N_2 RH<5 % N_2 RH 100 %	0.035 0.2	0.0125 0.1357	[78]

a-C:H film in vacuum. In dry nitrogen (10^5 Pa, RH <1%), similar friction values were measured. Verkammen et al. [134] measured low friction values for the PACVD deposited a-C:H films sliding against steel in the range 0.003–0.009 in vacuum (2×10^{-6} mbar) and 0.006–0.015 in dry nitrogen. The film wear rates were in the range 2.2×10^{-6} to 7.8×10^{-6} $mm^3(Nm)^{-1}$ and 0.026×10^{-6} to 0.091×10^{-6} $mm^3(Nm)^{-1}$, respectively. Both the friction and wear could be reduced by using a-C:H coated pin sliding against the a-C:H coating reaching friction values in the range 0.002–0.09 in different atmospheres.

Extremely low friction values have been measured for the highly hydrogenated DLC films deposited by PACVD. The superlow friction values, 0.003–0.005, were measured by Erdemir et al. [30] when sliding DLC against DLC in dry nitrogen. The superlubricity is related to adhesive friction on a molecular scale and thus it is necessary to avoid friction occurring on the macro- and microscale. The ploughing friction can be avoided by using hard substrates, and the asperity collisions can be avoided by using nanosmooth surfaces, like polished Si wafers, sapphire or cleaved mica surfaces. The effect of surface roughness on friction was shown by Erdemir, as he reported the friction evolution for the same hydrogenated DLC film deposited on two substrates with different surface roughness. The rougher steel disc (R_a = 20 nm) performed higher friction in dry nitrogen (0.007) compared to the film deposited on smooth (R_a = 0.7 nm) sapphire disc (0.003) as represented in Fig. 3 [20].

According to Donnet et al. [14] the nanosmooth surfaces can be generated between two smooth DLC coatings or between the DLC film and the transfer layer formed on the sliding counter surface.

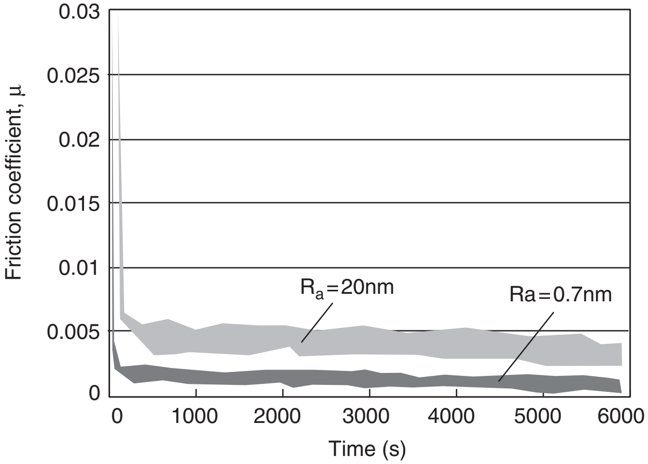

Fig. 3 Friction coefficient of highly hydrogenated DLC films deposited on steel (R_a = 0.020 μm) and on sapphire (R_a = 0.0007 μm) substrates. Tests were carried out in dry nitrogen, with load of 10 N and sliding velocity of 0.3 ms^{-1}. (After [20].)

Donnet and Grill reviewed the influence of coating properties on the friction performance of a-C:H films in UHV. Ultra-low friction (μ <0.01) was reached, when the hydrogen content of the film was high enough (about 40 at. %), the carbon network was sufficiently cross-linked and the film structure had a noticeable fraction of hydrogen unbonded to carbon [11]. The minimum hydrogen content required for the superlow friction performance in UHV was later explained to be dependant also on the deposition method employed by Sánchez-López et al. [123].

Erdemir et al. observed the tribological performance of hydrogenated a-C:H films deposited by PACVD technique to be changed according to the source gas composition used in deposition. The lowest friction performance in dry nitrogen atmosphere was measured for the DLC against DLC contact, when the films were obtained with gas compositions having high hydrogen to carbon ratio. The superlow friction values, in the range 0.003, were measured for the films derived from the gas mixture of 25% methane and 75% hydrogen. The coating was highly hydrogenated and it was named nearly frictionless carbon (NFC). With increasing amounts of hydrogen in the source gas mixture, the wear rate of the coating also decreased in dry nitrogen, accompanied by decreasing friction. In ambient humid environment (26–44% RH) similar friction coefficient values in the range 0.1–0.2 were measured for the films deposited with different source gas mixtures [28–30].

Sánchez-López et al. [123] suggested the viscoplastic behaviour of the coating being an indicator for predicting the friction performance of the coatings in UHV. The presence of unbonded hydrogen trapped in the structure of the coating increases the viscoplasticity of the coating and decreases the hardness of the coating. Fontaine et al. [33,34] determining the viscoplastic exponent for a-C:H coatings and established a correlation between superlow friction and viscoplasticity for the a-C:H films. The authors also suggested the possibility to control the viscoplaticity and hardness of the coating independently in order to obtain high hardness with superlow friction performance.

3.1.2 The Effect of Hydrogen in Inert Environment

Hydrogen has been shown to play a key role in the tribological performance of hydrogenated DLC films in an inert environment. Already Paulmier et al. [108] reported the reduction of friction caused by the adsorption of atomic hydrogen on the DLC surface as the adsorbed hydrogen decreased the chemical activity of DLC film. Further Zaidi et al. [145,146] and Le Huu et al. [72,73] observed that H^+ was desorbed while tribotesting the DLC film in vacuum, but a small quantity of water vapour stopped the desorption of H^+. The authors claimed the hydrogen to be weakly bonded in C–H bonds under vacuum conditions and desorption of hydrogen to occur at low temperatures due to frictional heating. Hydrogen was claimed to act as a lubricant reservoir reducing the friction, but at the same time increasing the wear.

Donnet et al. studied the friction performance of DLC coatings with hydrogen content of 34 at. % in UHV and noticed that the coating experienced a drastic increase of friction in vacuum after a short period of superlow (0.005) friction. This high friction in inert atmosphere could be reduced by introducing at least 1 kPa of hydrogen gas in the vacuum chamber as represented in Fig. 4. The low friction performance could be further enhanced by increasing the test temperature in order to enhance the diffusion of hydrogen species. The effect of hydrogen was attributed to the favourable friction process on the molecular scale due to systematic formation of a carbonaceous transfer film during the tribological test. The sliding was explained to occur between the two nanosmooth contact surfaces, namely the deposited films and the transfer film [14].

Fontaine et al. also used hydrogen to control the friction performance of a-C:H films in inert atmospheres. The intermediate and high hydrogen pressures (100–1,000 Pa) were observed to provide a healing effect on the transfer layer and the superlow friction performance of the a-C:H film with low intrinsic hydrogen content. The authors also noticed the effect of the oxide layer formed on the counter surface. This oxide layer had to be removed either by etching or by sliding action, in order to allow the favourable reaction between carbon and metallic iron to occur, leading to build-up of the transfer film [33–35].

The superlow friction performance of highly hydrogenated a-C:H films in dry nitrogen is explained to be governed by the presence of hydrogen. On the surface

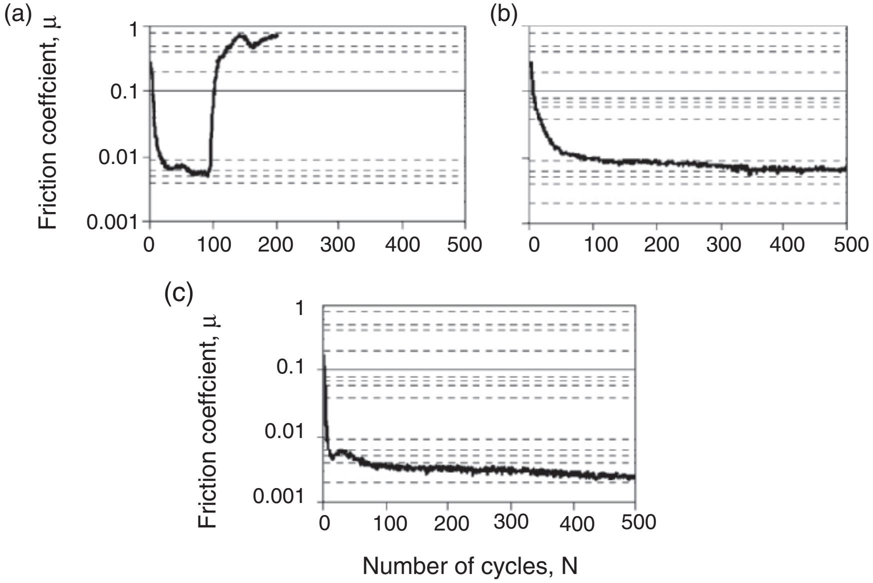

Fig. 4 Friction coefficient as a function of sliding cycles of hydrogenated (34 at. % H) DLC film tested (a) in UHV conditions at room temperature (25°C) and in atmosphere of pure hydrogen (1 kPa) (b) at room temperature (25°C) and (c) at 150°C. (After [14].)

of films prepared in highly hydrogenated plasmas, the carbon atoms are strongly bonded to hydrogen, eliminating the free σ-bonds on the surface. Some carbon atoms are also believed to be dihydrogenated (i.e. two hydrogen atoms bonded to one carbon atom), with sliding occurring between two hydrogen-terminated surfaces providing superlubricity in inert atmosphere, e.g. in dry nitrogen. Atomic and/or molecular hydrogen within the films can also serve as a reservoir that can continuously replenish and terminate the σ-bonds that can be exposed by mechanical wear or thermal desorption [19,20].

The superlow friction performance of hydrogenated DLC films in inert environments is thus attributed to the hydrogen-terminated surfaces interacting through weak van der Waals forces. According to Gardos, these hydrogen-terminated bonds have a low bonding strength of about 0.08 eV per bond. In the humid oxygen-containing environment, the coefficient of friction increases, which corresponds to an increase in bond strength from about 0.08 eV per bond to about 0.21 eV per bond, which is typical for hydrogen bonding of water molecules at C=O sites [39].

3.1.3 The Effect of Gas Adsorption in Inert Environment

The adsorption of gasses on hydrogenated DLC film surface has been observed to have an influence on the friction performance in an inert environment. In the tests performed in dry nitrogen, and in vacuum, against steel (AISI 52100), the friction coefficient of a-C:H film varied from 0.003 to 0.009 in vacuum (2×10^{-6} mbar) and from 0.006 to 0.015 in dry nitrogen. The dependence of dwell period and sliding speed was observed to have an influence on the friction performance in dry nitrogen and in vacuum. The steady-state friction was a function of sliding speed and decreased with increasing speed. The static friction was observed to be a function of the dwell period increasing with increasing dwell period, which was attributed to adsorption phenomena. The tests in ambient air did not show a similar effect [134].

The effect of gas adsorption on the highly hydrogenated DLC films was studied by tribotesting in dry nitrogen by Heimberg and co-authors. With sliding speeds 0.1 mms^{-1} and higher superlow friction coefficient values (0.003–0.008) were measured, but as the sliding speed reduced, the friction coefficient increased to values typically measured in ambient air (0.01–0.1). Tests with different time-delays between sliding cycles showed increasing friction coefficient as the exposure time was increased as shown in Fig. 5. The superlow friction could be sustained, suppressed and recovered as a function of exposure time. The rise in friction coefficient was found to be in good quantitative agreement with the adsorption kinetics predicted by Elcovich equation for gas adsorption onto carbon [49].

A model of fractional coverage based on the adsorption of environmental contaminants and their removal through the sliding contact was developed by Dickrell et al. [9]. The model was found to fit the experimental friction data

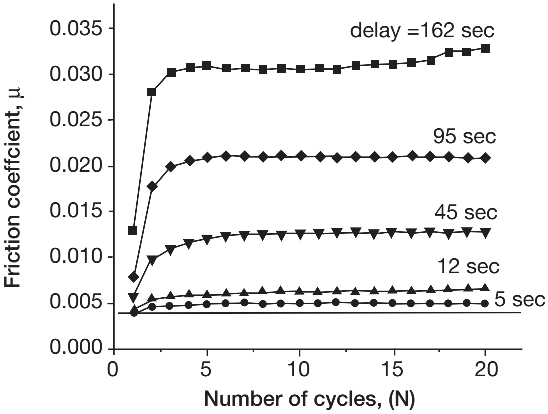

Fig. 5 The friction coefficient of highly hydrogenated DLC film is shown as a function of reinitialized cycle number for five different time delays. The solid line indicates the friction coefficient measured in the continuous high speed test (≥1 mms^{-1}) with friction coefficient of 0.004. (After [49].)

with a constant deposition rate of adsorbates, if the removal fraction increased with increasing speed and decreasing dwell time. The computer simulations by Borodich and Keer also suggested microscopic processes, such as breaking and forming of interatomic bonds, to affect macroscopic phenomena, like friction. In addition, the initial roughness of the DLC surface was suggested to considerably influence the probability of breaking bonds during mechanical removal of adsorbates, and on the process of the gradual tribochemical wear of DLC films [6].

3.2 The Friction and Wear Performance of Hydrogenated DLC Films in Ambient Air and Humid Environments

The hydrogenated DLC films are known to be sensitive to the presence of oxidizing elements, like water vapour and oxygen, and the friction coefficient in ambient air is typically higher than in inert environments. The friction coefficient values of 0.005–0.02 measured for the hydrogenated DLC films sliding against steel in vacuum (p_{H_2O} = 10^{-8} Torr) increase up to values in the range 0.2 as the partial pressure of water vapour is increased as shown in Fig. 6.

A similar trend was also observed in nitrogen atmosphere when the relative humidity increased [17,18]. According to Donnet et al. [15] the friction is strongly influenced by water vapour at partial pressures higher than 0.05 kPa (2% RH) increasing the friction coefficient up to 0.15 accompanied by severe wear. The typical values of friction coefficient reported for hydrogenated DLC films

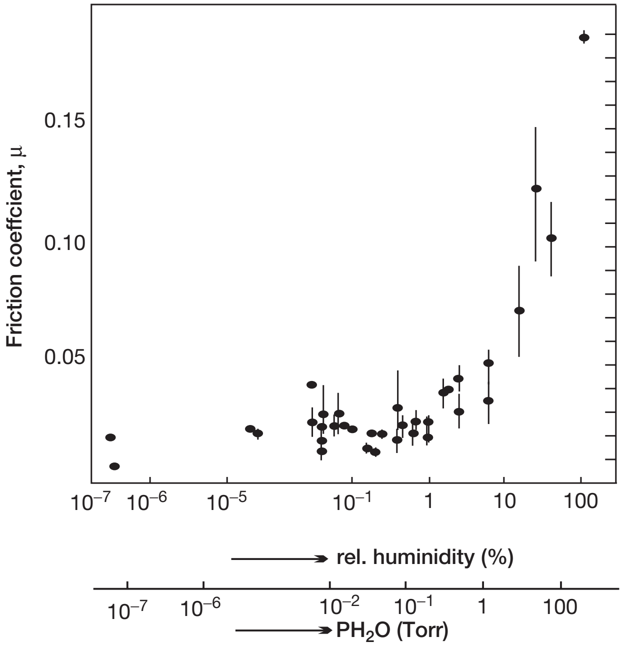

Fig. 6 The friction coefficient (μ) of hydrogenated DLC film sliding against steel pin as the relative humidity is increased. (After [18].)

sliding in ambient air against steel are in the range 0.1–0.3 and against ceramic materials in the range 0.02–0.15 (Table 2).

The friction coefficient values of highly hydrogenated DLC films tested against themselves in UHV also increased from superlow value 0.004, when H_2O or O_2 was introduced in the chamber. As described in Fig. 7 the friction coefficient started to increase with H_2O vapour pressure exceeding 0.01 Torr (1.3 Pa) and increased up to 0.07 with vapour pressure 10 Torr (1.3×10^3 Pa) representing about 50% RH. The O_2 pressure had an analogous effect on friction performance, but higher O_2 pressure was required in order to induce a similar increase in friction. The N_2 gas has hardly any effect on the friction. Under H_2O vapour pressure, the friction increase may be caused by the adsorbed layer of H_2O molecules covering the film surface and increasing the dipole-like interaction of the DLC film interfaces. The friction changes were reversible and no evidence on tribochemistry was observed by Auger Electron Spectroscopy (AES). In the case of hydrogenated DLC sliding against hydrogenated DLC, the friction changes are suggested to be dominated by weakly physisorbed gas molecules [3,4,20,62].

Similar increase in friction coefficient with increasing humidity and with the presence of oxygen has been observed by Li et al. [78] in tests carried out with steel balls (AISI 52100) against hydrogenated DLC. The tests carried out in humid

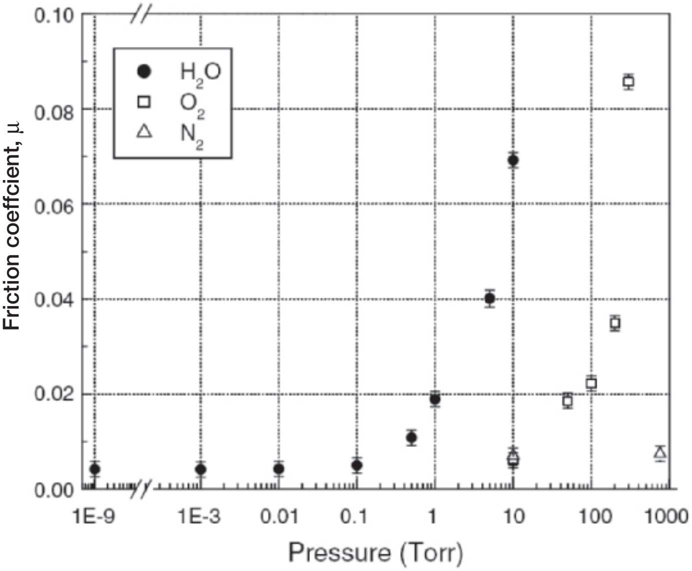

Fig. 7 Friction coefficient of a highly hydrogenated DLC films under varying pressures of H_2O, O_2 and N_2. (After [62].)

air (40% RH), humid nitrogen (40% and 100% RH), dry oxygen (<5% RH) and dry nitrogen (<5% RH) showed low friction coefficient in dry nitrogen, but increased friction for increased humidity. The highest friction was experienced in oxygen atmosphere. The increasing humidity was also observed to increase the wear rate of the DLC film as shown in Fig. 8 for the N_2 environment.

Under humid conditions water molecules are expected to cover the surface. The studies on the effect of water adsorption on DLC films carried out by Tagawa et al. [129] showed that the hydrogenated DLC films had a higher advancing contact angle of water (83–97°) compared to hydrogen-free DLC films (77°) measured by quartz crystal microbalance (QCM). The hydrogen termination of the dangling bonds on hydrogenated DLC film surface increases the contact angle of water, thus leading to decreased adhesion force and to lower friction. The adhesion force measured by an environment-controlled microtribometre reached the highest values for the W-tip sliding against hydrogenated DLC films deposited on Si, with relative humidity values of 40–60%, which represents water coverage of a few molecular layers between contacting surfaces.

In the case where the water molecules are weakly adsorbed on the hydrogenated DLC surface, they can be easily displaced by, e.g. the sliding counterpart. The effect of sliding speed on friction coefficient was observed to have a decreasing trend in tests carried out in humid air (50% RH) with hydrogenated DLC films sliding against steel (AISI 52100) or Al_2O_3 balls. The friction coefficient decreased from 0.42 to 0.10 against steel and from 0.10 to 0.02 against alumina, as the sliding speed increased from 0.1 to 3 ms^{-1} [114] The influence of sliding speed was also

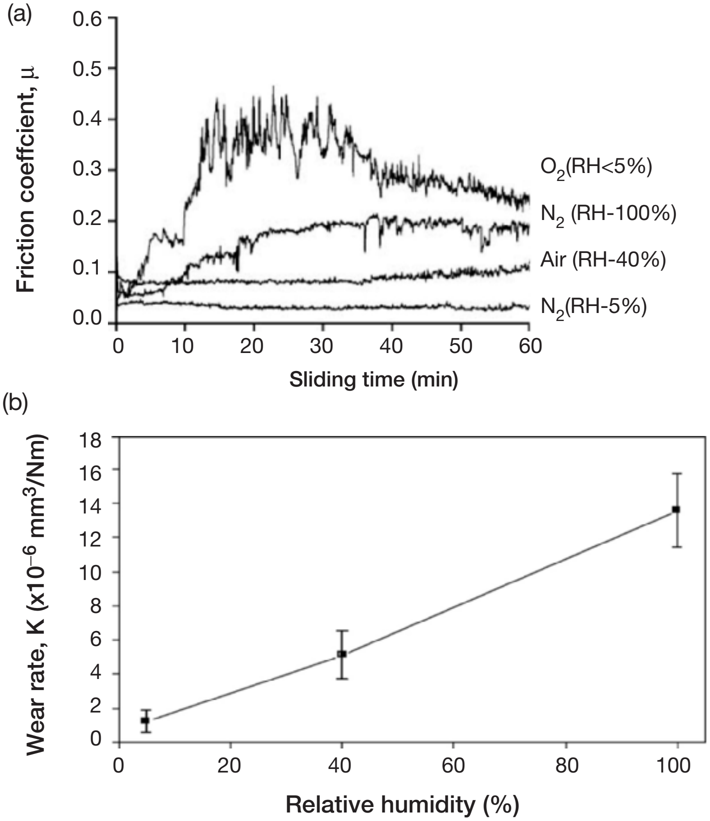

Fig. 8 (a) The friction coefficient of hydrogenated DLC film at different relative humidity in nitrogen environment (<5, 100% RH) and O_2 (<5% RH) environment and in humid air (40% RH), and (b) the wear rates of DLC film at different relative humidity in nitrogen environment. The steel pin was slid against the DLC film with a normal load of 2 N and the sliding velocity of 2 ms^{-1}. (After [75,77].)

verified in sliding tests carried out under different H_2O pressures. The results showed that higher H_2O pressure required higher sliding velocity to exhibit a similar decrease in friction compared to lower pressure conditions [62].

The tribological tests carried out in ambient air (25–40% RH) with reciprocating pin-on-flat test configuration by Sánchez-López et al. [123] showed that the wear resistance of hydrogenated DLC films is related to the intrinsic structural film properties that are controlled by the deposition conditions. It was observed that the best wear resistance of DLC films was related to higher hardness and higher Young's modulus accompanied with a lower amount of hydrogen in the structure. The hardness and Young's modulus is increased as the hydrogen content decreases combined with the higher cross-linking of the carbon network in the hydrogenated DLC film.

3.2.1 Formation of Transfer Layer

A frequently observed feature in tribological testing of DLC films is the formation of transfer layer. Formation of a transfer layer has been reported from the early days of DLC research by, e.g. Memming et al. [89], Miyoshi et al. [98], Sugimoto and Miyake [126] among the first authors. The formation of carbonous transfer layer on the sliding surface was observed to reduce the friction coefficient. A drastic decrease in friction was reported by Miyoshi [98] as a layer of reaction products was formed. In another case, the friction reduction was observed as the transfer of hydrocarbons with a specific orientation to the ball surface was generated [126]. The formation of transfer layer has been observed to be enhanced by the increased sliding distance (20–25 km) leading to friction reduction (from 0.16 to 0.05–0.07) [25,88]. Moreover, the sliding speed has been observed to enhance the layer formation as shown in Fig. 9, where the largest and most compact transfer layer was observed for high load and high sliding speed. The thick layer formation was also observed to decrease the wear rate of the hydrogenated DLC film and the steel pin sliding against the coated surface [117]. The transfer layer formation is typically observed in tests carried out in ambient air, but also in UHV when the DLC film was sliding against steel [13].

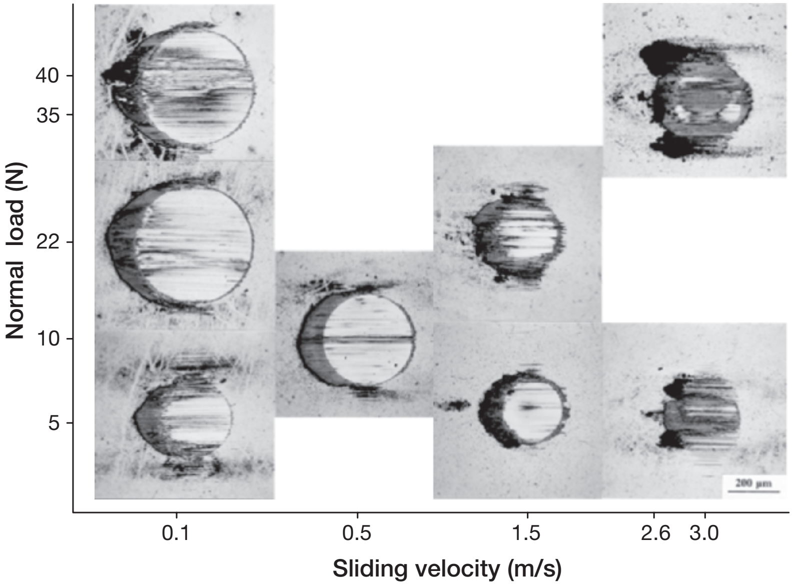

Fig. 9 The wear surfaces of the steel pins slid against the PACVD deposited hydrogenated a-C:H film. The sliding speed was varied in the range 0.1–3.0 ms^{-1} and the normal load in the range 5–40 N

3.2.2 The Graphitization of the Hydrogenated DLC Film Structure

The micrographitization was suggested to be responsible for the low friction performance of DLC films by [56]. In 1993, Wei et al. [140] observed, by Raman analyses, the formation of disordered graphite on the wear surface of the hydrogenated DLC film due to fatigue wear in lubricated rolling-contact fatigue tests. Erdemir and co-workers discovered in pin-on-disc sliding tests carried out in dry nitrogen atmosphere, a transfer layer formation on the wear surface of a steel pin. The layer was rich in carbon and had a disordered graphitic structure as verified by micro-laser Raman spectroscopy [26]. Later, graphitization was also detected to occur in ambient atmosphere [83]. The mechanism was explained to occur as the accumulation of sliding-induced heat causing the gradual destabilization of C–H bonds in the hydrogenated tetrahedral structure.

Since hydrogen atoms are expected to promote the sp^3 bonding of the hydrogenated DLC structure, the release of hydrogen will destabilize the tetrahedral bonding and enhance the transformation of tetrahedral sp^3 structure to graphite-like sp^2 structure. The removal of hydrogen can, thus, trigger the transformation of the sp^3 structure into a graphite-like sp^2 structure. The transformation of hydrogenated DLC structure to graphite is thus suggested to gradually proceed at asperities due to repeated tribological contacts that lead to graphitization resulting in microcrystalline graphite [23,82,84,85]. Besides this wear- and friction-induced annealing on local contact areas, the sliding-induced strain energy can also further assist the transformation process [84].

The graphitization has been detected by several analysis techniques. Micro-laser Raman was used by several authors evidencing the presence of disordered graphite structure in the carbonous transfer layer or in the debris particles at sliding interfaces [26,79,83,121,151]. In Fig. 10, the micro-laser Raman spectra of the transfer layer and the wear debris generated in the tests carried out with steel pin sliding against DLC film reveal a similar structural chemistry to the crystalline graphite. The two broad Raman bands, at 1,336 and 1,594 cm^{-1}, match the D and G bands of crystalline graphite. The signal peaks of the transfer layer are not as sharp as that of the graphite, which is probably due to the small particle size, high structural disorder in the transfer layer and to phonon-damping effects.

Besides Raman analysis, the electron diffraction pattern analysis, FTIR analysis and bright-field/dark-field imaging has evidenced the presence of graphite in the tribocontact of hydrogenated DLC films [82,83,85]. The nanoindentation analysis also revealed that the transfer layer with a graphitic nature was characterized by lower values of Young's modulus (*E*) and hardness (*H*) compared to original coating. [110].

A higher sliding velocity was observed to enhance the friction reduction during tribotesting suggesting transformation of DLC to a graphitic state to be a direct consequence of frictional heating [27,14]. By using a software program,

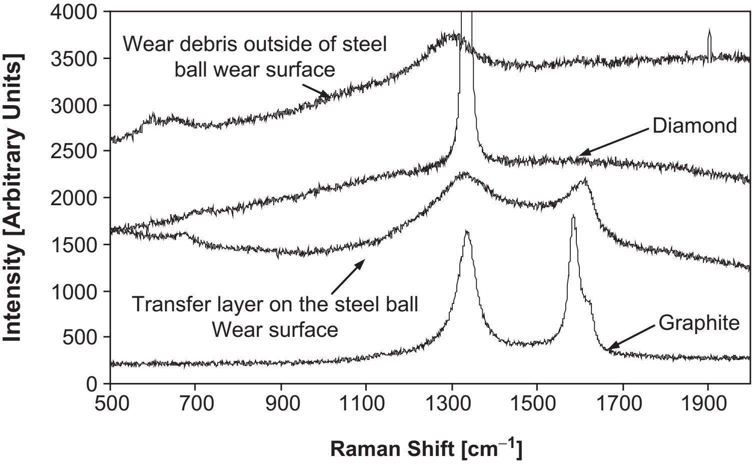

Fig. 10 Raman spectra of the transfer layer formed on the pin wear surface and the wear debris collected outside the wear surface of the steel pin. Raman spectra of the crystalline graphite is provided as a reference. (After [122].)

the flash temperatures generated at the contact asperities were estimated. When the steel pin was sliding against hydrogenated a-C:H with high load (up to 40 N) and sliding speed (up to 3 ms^{-1}), the flash temperature reached values in the range 350°C as calculated by Ronkainen and Varjus [27]. Other estimations carried out by using a simple model for asperity temperature rise, represented temperature values in the range 100–300°C for the metal pins and in the range 220–1,245°C for the ceramic pins sliding against hydrogenated DLC with an increasing trend for the repeated contacts [84]. The hydrogen effusion has been observed to occur in a-C:H films at elevated temperatures 300–600°C depending on the deposition parameters used for the coating deposition [141]. As the flash temperature on the surface asperities of DLC-coated surface is increased during repeated sliding, the hydrogen effusion is likely to occur and some of the DLC film structure will transform to graphite-like carbon.

The graphitization was observed to be sensitive to humidity effects. The low humidity level (0% RH) enhanced the graphitization rate due to reduction of the effect of water molecules, which could be observed as a shortening of the sliding distance required for the steady-state low friction performance and for the formation of graphitized tribolayer at low humidity conditions. Conversely, the graphitization rate decreased in high humidity (100% RH) and at lower temperature (−10°C) conditions [85].

3.2.3 Tribochemisty of Hydrogenated DLC Films

In humid environments and in ambient air, oxidizing species, like H_2O and O_2, are present, influencing the tribological performance of materials. The tests carried out at water vapour partial pressures of 1 hPa (4% RH) showed friction coefficient of 0.15 accompanied by severe wear reported by Donnet and co-workers. The authors observed wear particles consisting of ferrous oxides (Fe_2O_3) embedded in an amorphous carbon structure [15]. The influence of atomic oxygen was observed to influence the friction performance of hydrogenated DLC films more than molecular oxygen, by increasing the friction value from 0.08 measured in inert environment, up to 0.22. This was attributed to the higher sticking coefficient of atomic oxygen compared to the molecular oxygen, leading to increased chemical activity of the diamond-like coating due to adsorbed oxygen [108].

During tribological testing of DLC films in ambient air, occurrence of material transfer has been observed by several authors [36,96,107,118,119]. The SIMS analyses and Auger elemental imaging, for example, showed that a transfer layer consisting of carbon, iron, chromium and oxygen was formed when a steel pin was slid against the DLC film in humid (50% RH) air. When Al_2O_3 pin against hydrogenated DLC film was used, aluminum and oxygen together with carbon species were detected after sliding in humid air as detected by Ronkainen et al. [118,119].

In humid conditions, the surface interaction of the steel ball with water vapour seems to accelerate the surface oxidation of the steel ball, resulting in high concentration of iron (Fe) in the wear debris. The Auger analyses showed that the wear debris contained large amount of iron when a-C:H film was slid against steel counter body (AISI 52100) in humid air or in dry oxygen. The friction coefficient increase from 0.025 to 0.2 accompanied with the increase of Fe concentration in wear debris was detected by Park and co-authors as the humidity of the surrounding air increased from 0% to 90% RH as shown in Fig. 11. Moreover, in dry oxygen environment, the friction against steel was high (0.2–1.0) accompanied by the Fe incorporation in the wear debris. However, for the sapphire balls slid against a-C:H film in dry oxygen, low friction values (0.02–0.07) were detected, even though aluminum was detected in the wear debris [107].

Kim et al. reported the effects of oxygen and humidity on friction and wear of highly hydrogenated (55 at. % H) a-C:H films produced by PACVD. When the films were slid against silicon nitride ball in air and argon atmosphere with dry (<3% RH), intermediate (50% RH) and saturated (95% RH) humidity conditions, the friction coefficient increased from 0.06 to 0.19 as the humidity increased. In humid and oxygen atmospheres, the tribochemical reaction with DLC was observed, and oxidized hydrocarbon species (C=O) were created forming polymer-like wear debris, as detected by FTIR microprobe. This was verified at higher loads (9.8 N) [67]. For the low loads (7.8 kPa), the creation of C–O bonds was reported by Olsen et al. [105]. According to Zaidi et al. [144] oxygen forms various types of oxygenated complexes on the carbon surface as the film is in contact with the atmosphere. The formation of oxygen complexes is strongly dependent on the relative humidity, which might be the reason for the negative effect of humidity on the friction and wear performance of the hydrogenated carbon films. Oxidation of the unstable polymer-like surface layer could, therefore, be the main reason for the degradation of the frictional behaviour of the coating.

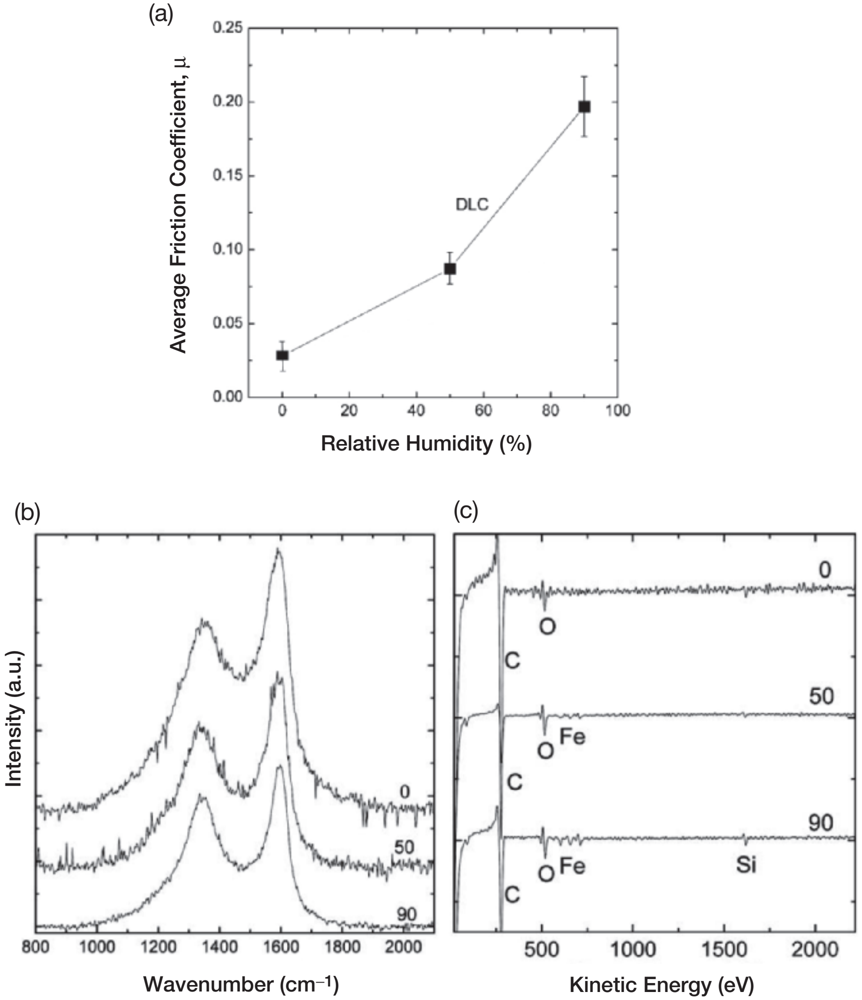

Fig. 11 (a) The dependence of the average friction coefficient of hydrogenated DLC film on relative humidity (0, 50 and 90% RH) in ambient air. (b) Raman spectra and (c) Auger spectra of the wear debris formed by sliding a steel ball against a DLC film in ambient air (0, 50 and 90% RH). (After [107].)

Fukui et al. [36] analysed the wear tracks and wear debris generated in the tribological tests carried out with a-C:H film sliding against steel pin in pin-on-disc tests in humid air (65% RH). According to the EDS spectra the wear debris contained carbon, oxygen and iron, and it was presumed that most of the powdery wear debris was generated by wear of the steel pin. According to the time-of-flight secondary ion mass spectroscopy (TOF-SIMS), high-order mass fragments were detected inside the wear track of the coating. The presence of mass numbers 42 (C_3H_6), 43 (C_2H_3O), 58 (C_4H_{10}), 84 (C_6H_{12}), 104 (C_7H_4O, C_8H_9), 138 ($C_6H_2O_4$), 149

($C_8H_5O_3$), 163 ($C_8H_{19}O_3$) and 219 ($C_{15}H_{23}O$) were found inside the wear track. These results differed from the original composition of the DLC film representing mass numbers 14 (CH_2) and 28 (C_2H_4). The presence of species with high-order mass numbers such as polymers (molecules of higher order hydrocarbons) inside the wear track assumes that polymerization occurs as the transfer layer is formed during tribotesting. These friction polymers contribute to the friction performance of hydrogenated DLC film in humid environment. Yoon et al. [143] also suggested the formation of a carboxylic acid soap when oxidized DLC films chemically reacted with ferrous oxide.

The tribological performance of DLC films in oxygen- and water-containing environments was explained to result from friction-induced physical and chemical interactions by Li and co-workers [76,77]. They carried out pin-on-disc tests with hydrogenated DLC films against steel in humid air (~40% RH), dry nitrogen (<5% RH), humid nitrogen (~100% RH) and dry oxygen (<5% RH). In dry nitrogen, the lowest friction coefficient was measured (0.035) with the formation of a carbon-rich transfer layer on the pin wear surface The worn DLC surface exhibits similar structure to the original film. However, in oxygen- and water-containing conditions, distinctive structural changes by x-ray photoelectron spectroscopy (XPS) was detected. On the worn surface, the concentration of oxygen was 3–4 times higher compared to the original film, and some traces of Fe species were also detected when oxygen or humidity were present. The XPS analysis of the wear surface of DLC film indicated the carbon 1s core level spectrum being shifted to a higher binding energy. The intensity of C–C (or C–H) decreased, while the intensity of C–O and C=O peaks increased and new peaks describing carboxylic acid (HO–C=O) groups were observed as shown in Fig. 12.

Li and co-workers further detected, by XPS analysis, Fe–C bonds on DLC wear surface after tribotesting DLC against steel in humid nitrogen and dry oxygen conditions, and Fe–O bonds after tests in dry oxygen. The concentration of oxygen elements and the intensity of C–O and C=O bonds indicated the cracking of the film chains and the oxidation of DLC film. The broken C–C and C–H bonds form macro-radicals, which in the presence of water or oxygen, would chemisorb water or oxygen molecules to form peroxide radicals (ROO*). The peroxide radicals could remove hydrogen atoms from water molecules or molecular chains of DLC film and form hydroperoxide groups (–COOH). Radicals could also react with water or oxygen molecules directly and generate peroxide radicals (R′OO*), which would react again. These processes, which are described in Fig. 13, will be repeated until the carbon network is terminated [75,77].

The friction-induced oxidation changes the surface chemical states from C–H bonds to oxygen-containing groups, which means an increase in the bonding strength from 0.08 eV per bond related to the van der Waals bonding, to about 0.21 eV per bond for the C–O and C=O sites. This results in increased friction values in humid environment [39]. The macro-radicals could also react with activated Fe atoms to form Fe–C bonds under frictional shearing action. The peroxide radicals could also react with Fe atoms to form ROO–Fe bonds. These interactions will lead to strong adhesive friction. Since the temperature at the

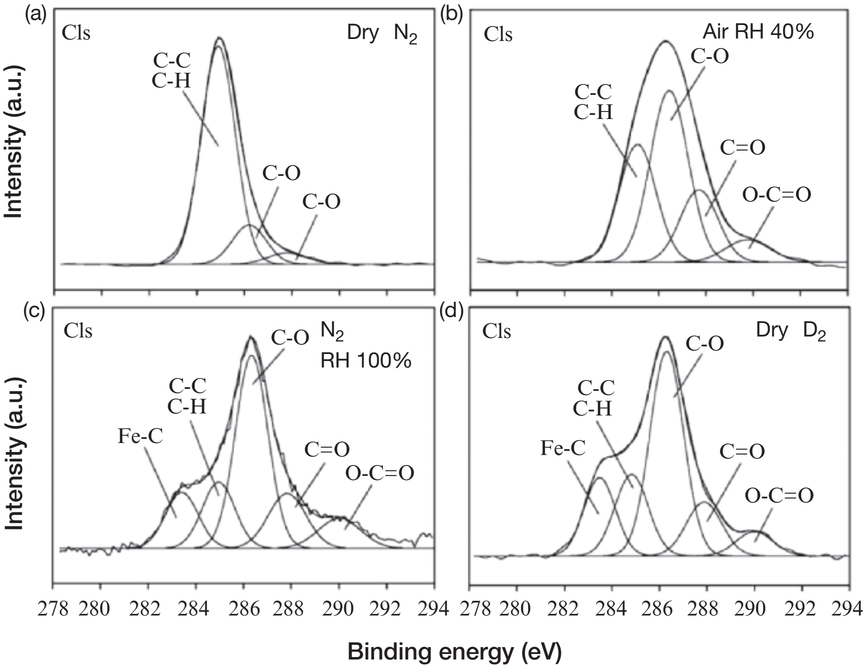

Fig. 12 The XPS spectra for carbon 1s states on the worn surface of hydrogenated DLC film tested in different environments, (a) in dry nitrogen (RH <5%), (b) in humid air (about 40% RH), (c) in humid nitrogen (about 100% RH) and (d) in dry oxygen (<5% RH). (After [75].)

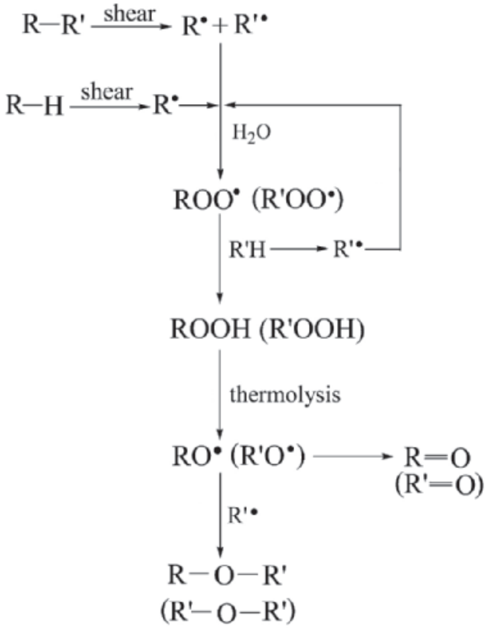

Fig. 13 Schematic diagram of the cracking and oxidation processes of DLC film during friction testing in humid environment. (After [77].)

surface asperities will increase during sliding action (about 100–300°C) Fe can react with water and oxygen forming Fe species, Fe_2O_3, Fe_3O_4 and FeOOH, in the tribocontact [77].

When DLC film is sliding against Si_3N_4, silica gel formation has been observed on the worn surface due to the oxidation and hydrolysis of the Si_3N_4 ball, which resulted in low friction (0.085) in humid nitrogen. The Al_2O_3 counter material, on the other hand, catalyzed the degradation of DLC causing high wear of DLC coating as detected by Li et al. [76]. The authors concluded that in oxygen- and/or water-containing environments the formation of the transferred carbon-rich layer on the steel ball was inhibited by the friction-induced chemical reaction and oxidation of the hydrogenated DLC film.

3.2.4 The Influence of Doping on the Tribological Performance of Hydrogenated DLC Films in Ambient Environment

Since the tribological performance of hydrogenated DLC films is greatly influenced by the environmental aspects, doping and alloying has been used to modify some of the surface-related properties, and to overcome the tribological limitations. Typical alloying elements used to influence the tribological performance, are silicon, fluorine, nitrogen and different metals.

Silicon incorporation in a-C:H structure affects most coating properties, including surface energy and internal stresses, and is therefore often used to stabilize the friction performance of a-C:H coating in humid atmosphere. The friction coefficient of Si-doped a-C:H film appears to be significantly reduced, below 0.1, compared to an undoped a-C:H film in ambient air as reported, e.g. by Oguri and Arai [103], Itoh et al. [55] and Miyake and Kaneko [92]. As Meneve and co-authors studied the behaviour of a-Si_{1-x}:C_xH films ($0.7 < x < 0.9$), they noticed that in humid conditions the potential applications will be limited to contact pressures below 1 GPa due to the lower wear resistance of the Si-doped coating [90].

Gilmore and Hauert received similar results, since the coating wear increased by a factor of 2–4 when the Si content increased from 1 to 6 at. %. Simultaneously, the Si doping reduced the friction in high humidity environment by a factor of three compared to undoped DLC. The friction coefficient of Si-doped DLC coating could be held approximately constant at 0.08 ± 0.01 over the humidity range 5–85% with a 4 at. % Si-doping [40]. The Auger spectroscopy of Si-doped DLC films revealed the formation of Si-rich oxide debris and the low and stable friction performance was related to sliding between hydrated silica debris on both coating and counterpart surfaces [63].

Multilayer coatings consisting of a stack of Si-doped nanocomposite DLC layers provide stress relief, enabling the deposition of thick layers without loss of adhesion. The multilayer films showed low friction (<0.1) regardless of the humidity also providing an improved abrasion resistance [8]. The nanocomposite DLC resulted in friction coefficients typically between 0.05 and 0.15 even in humid air [100,101].

Different gas species have also been used for doping DLC films. Fluorine incorporation in the a-C:H structure affects the surface properties and reduces the internal stresses. The combination of Si and F in a a-C:F:Si:H film structure can further improve the tribological performance of Si-doped coating [93]. On the other hand, F-incorporation was found to increase the friction against steel up to 0.9 in dry environment [41]. The friction performance of the Ar- and N-incorporated DLC films have shown low friction performance typically in the range 0.05–0.18 with low wear rate in different environments [148].

The DLC films have also been doped with several different metals, such as Ti, Nb, Ta, Cr, Mo, W, Ru, Fe, Co, Ni, Al, Cu and Ag. The compressive stresses are typically reduced to values below 1 GPa. The metal-alloyed a-C:H structures exhibit steady-state friction values in the range 0.10–0.20 with slight dependence on the humidity. The tribological behaviour of these metal-alloyed a-C:H films has been explained by a combination of ceramic-like properties (high hardness) and polymer-like properties (high elasticity, low surface energy) [11].

3.3 The Friction and Wear Performance of Hydrogen-Free DLC Coatings in Ambient Air and in Humid Environment

Hydrogen-free DLC films can be divided into two major groups according to the bond structure of the film. The tetrahedral amorphous carbon (ta-C) films are highly sp^3 bonded providing the film with diamond-like properties, such as high hardness and chemical inertness. The ta-C films can be deposited by different techniques, e.g. arc discharge or laser ablation. The amorphous hydrogen-free films (a-C) produced by magnetron sputtering are mostly sp^2 bonded, and therefore have different tribological performance compared to ta-C.

In humid environments, the ta-C films have a rather stable friction performance showing friction coefficient values typically in the range 0.1–0.2 against different counterface materials as shown in Table 3. The wear rates vary from 0.001×10^{-6} $mm^3(Nm)^{-1}$ to 0.1×10^{-6} $mm^3(Nm)^{-1}$ depending on the deposition method and deposition parameters used. The amorphous a-C films have similar friction performance to ta-C films, but the wear rates are higher for the a-C coatings compared to ta-C coatings.

Hirvonen and co-authors deposited ta-C films by an ion beam technique. The films had a steady-state friction coefficient of 0.14 against steel and 0.06 against silicon nitride in pin-on-disc tests carried out in ambient air [50]. The ta-C films deposited by arc-discharge method showed friction coefficient values in the range 0.12–0.2 against steel with an increasing trend as the sliding proceeded. The wear rate of ta-C coatings was in the range $0.07 \cdot\times 10^{-6}$ $mm^3(Nm)^{-1}$ against steel. Hirvonen et al. [51,52] reported the tribological performance of the ta-C film to be dominated by the formation of a carbon-rich transfer layer onto the counterface. The surface roughness of the films influenced the friction performance of ta-C coatings, since the films deposited by using a curved solenoid to filter the

Table 3 The friction coefficient values and the wear rates of the hydrogen-free DLC coatings tested in different environments

DLC film		Tribological testing						
Film (substrate)	Deposition technique	Countermaterial	Load (N)/(GPa)	Speed (ms^{-1})	Environment	Friction	Wear rate (x10^{-6} $mm^3(Nm)^{-1}$)	Reference Author year
ta-C (WC-Co)	Ion beam deposition	Steel	0.95 GPa	0.13	Ambient air	0.13	–	[50]
		Si_3N_4	1.23 GPa			0.06		
ta-C (Tool steel)	Vacuum arc discharge	AISI52100	0.86 GPa	0.1	Ambient air (40% RH)	0.12–0.22	0.07	[51,52]
ta-C (Steel)	Vacuum arc discharge	ta-C (Steel)	10–80 N	0.1–6.0	Ambient air (10^5 Pa)	0.04–0.13	–	[2]
					Vacuum (10^{-5} Pa)	0.6		
ta-C (Si)	Pulsed arc discharge	Si_3N_4	1.54 N	0.1	Ambient air (72% RH)	0.07	0.15	[67]
ta-C (Si)	Pulsed arc discharge	AISI 52100	5–20 N	0.1	Ambient air (50% RH)	0.26–0.17	<0.01	[115]
		M50	10 N	0.1		0.22	<0.01	
		Al_2O_3	5 N	0.1		0.21	0.06	
ta-C (Si)	Pulsed arc discharge	AISI 52100	10 N	0.1	Amb. air (20% RH)	0.4	0.008	[116]
					Amb air (50% RH)	0.19	0.007	
					Amb.air (70% RH)	0.2	0.01	
		Al_2O_3	5 N	0.1	Amb. air (10% RH)	0.26	0.07	
					Amb air (50% RH)	0.17	0.04	
					Amb.air (70% RH)	0.2	0.09	
ta-C (AISI 440B)	Pulsed arc discharge	AISI 52100	5–35 N	0.1–3	Ambienta air (50% RH)	0.14–0.19	0.03–0.16	[118]
		Al_2O_3				0.1–0.14	0.04–0.11	
ta-C (AISI440C))	Pulsed laser deposition	AISI440C/ Sapphire	0.98 N/0.8–1.1 GPa	0.2	Air (50% RH)	0.12/0.09	0.001	[137]
					N_2 (<2% RH)	0.10/0.08		
					Vacuum (10^{-7} Pa)	-/0.5		

(continued)

Table 3 (continued)

DLC film		Tribological testing						
Film (substrate)	Deposition technique	Countermaterial	Load (N)/(GPa)	Speed (ms^{-1})	Environment	Friction	Wear rate (x10^{-6} $mm^3(Nm)^{-1}$)	Reference Author year
ta-C (AISI 440B)	Pulsed arc discharge	AISI 52100	5N/0.8 GPa	0.02	Dry air (<3% RH)	0.66	–	[121]
					Dry N_2	0.61		
ta-C (AISI 440B)	Pulsed arc discharge	AISI 52100	5N/0.8 GPa	0.02	Dry air (<3% RH)	0.72	–	[71]
ta-C (Steel)	Pulsed vacuum arc	AISI 52100	2.5	0.01	Ambient air	0.35–0.1	–	[1]
ta-C (AISI H13)	Arc-PVD	AISI 52100	10 N/1.04 GPa	0.1	Dry N_2	0.6–0.7	–	[124]
					Dry air	0.3–0.7		
					Amb. air (40% RH)	0.14		
ta-C (AISI H13)	Cathodic arc evaporation	ta-C (M50)	1 N	0.07–0.03	Vacuum	0.65	–	[3,4]
					O_2	0.25		
					H_2	0.15		
					Humidity (50% RH)	0.07		
ta-C (AISI 440C)	Pulsed laser deposition	AISI 440C/SiC	1 N	0.125–0.2	Amb. air (40% RH)	0.11/0.12	against SiC: 0.2	[138]
					Dry N_2	-/0.05–0.7	against SiC: 8	
	Filt. cathodic vacuum arc	AISI 440C/SiC	1 N	0.125–0.2	Amb. air (40% RH)	0.1/0.11	against SiC: 0.1	
					Dry N_2	-/0.09–0.7	against SiC: 9	
ta-C (Ti-alloy)	Arc discharge	AISI 52100	2 N	0.02	Vacuum (<10^{-3} Pa)	0.34–0.41		[91]
					Amb. air (40%RH)	0.12–0.23		
a-C (Tool steel)	Magnetron sputtering	WC	25 N	0.048–0.45	Dry air (about 7% RH)	–	0.04–0.14	[57]
a-C (AISI52100)	Sputtering	Steel	5 N	0.07	Ambient air (30–40% RH)	0.2	0.06	[102]
a-C (HSS)	Magnetron sputtering	WC-Co	40–80 N	0.4	Ambient air	≤0.1	0.021–0.043	[31]

macroparticles during the deposition, resulted in friction values down to 0.07 when slid against Si_3N_4 pin [67].

The ta-C coatings deposited by pulsed vacuum arc-discharge method, having a predominantly sp^3 (66%)-bonded structure and containing less than 1 at. % hydrogen, are hard (54 GPa) with a high Young's modulus (445 GPa). In ambient air (50% RH), the wear rates of the coatings varied from 10^{-9} to 10^{-10} mm^3 $(Nm)^{-1}$ [67, 70,115,122].

The friction performance of the ta-C films studied by Ronkainen and co-workers with different normal loads (5–35 N) and sliding velocities (0.1–3.0 ms^{-1}) was stable showing friction coefficient in the range 0.14–0.19 against steel pin and in the range 0.1–0.14 against Al_2O_3 in humid air (50% RH), as shown in Fig. 14. The highest friction value (0.23) was measured for the high load and high sliding speed combination (35 N, 2.6 ms^{-1}). This was caused by the high local temperature generated in the sliding contact, which was verified by flash temperature calculations to be around 700°C. The high temperature presumably reduced the amount of water vapour in the sliding contact causing an increase in friction [118].

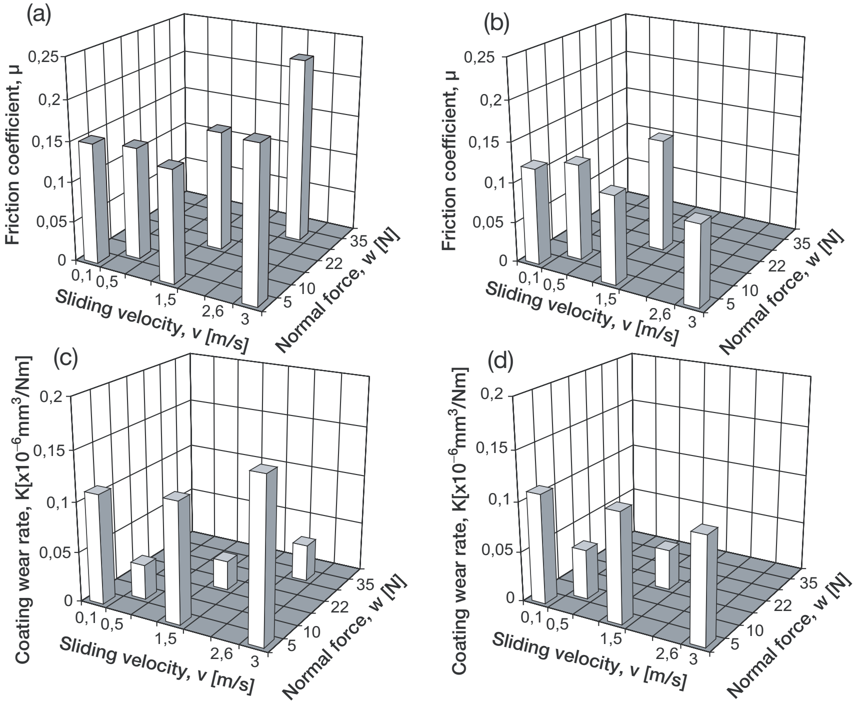

Fig. 14 The friction coefficient of ta-C film sliding against (a) steel and (b) Al_2O_3 balls and the coating wear rates against (c) steel and (d) Al_2O_3 balls in pin-on-disc tests with different normal loads (5–35 N) and sliding velocities (0.1–3 ms^{-1}). (After [118].)

The wear rates of ta-C films were typically lower than that of a-C:H films tested in similar test conditions. On the other hand, the wear rates of the counterparts were higher for the pins sliding against the ta-C coating due to slightly higher surface roughness of ta-C coating [115,117]. A transfer layer was formed on the steel pin (AISI 52100) wear surface that contained carbon and oxygen detected by secondary ion mass spectrometry (SIMS). On the wear surface of the coating, SIMS depth profiling and elemental imaging revealed a transfer of pin materials, iron and chromium. The amount of these species tended to increase as the sliding distance was increased up to 25 km accompanied with the increase in friction from 0.19 to 0.53 [116]. The micro-Raman analyses of worn surfaces of ta-C films indicated resemblance of graphite on the wear track of ta-C coating after a 5,400 m sliding against steel or Al_2O_3 [122]. In a similar way, the structure of ta-C film deposited by filtered cathodic vacuum arc was transformed to polycrystalline graphite, as detected by [125].

The hydrogen-free DLC films deposited by pulsed laser deposition (PLD) showed similar friction and wear properties compared to arc-discharge deposited ones. As determined by Voevodin et al. [135,137,139], the friction coefficient measured for the ta-C coatings against sapphire was in the range 0.07–0.10, and around 0.2 against steel due to chemical interaction of ta-C with steel. In the tests carried out in different atmospheres, namely ambient air (50% RH), dry nitrogen (<2% RH) and low vacuum (10 Pa of water vapour), the friction coefficient was observed to be nearly independent of the environment, since in all cases some water vapour was present in the test environment. The amount of humidity influenced the steady-state friction of ta-C films the most, showing a decreasing trend as the humidity was increased from 5% to 80% RH. The transfer film formed on the wear surface of hydrogen-free DLC film was suggested to be necessary for the low friction performance, and the graphite-like structure was detected in the transfer film after several thousands of sliding cycles. The Raman spectra showed the transformation of film structure from tetrahedral amorphous DLC to polycrystalline graphite as depicted in wear debris in Fig. 15 [137].

Due to high thermal stability (up to 400°C) of the PLD ta-C film, the thermally induced sp^3 to sp^2 transition was not possible according to Voevodin and co-workers. However, the high local pressures and the shear stresses acting on the coating surface during sliding could induce relaxation of the metastable sp^3 phase into sp^2 phase. The wear rates measured for the ta-C coatings were low, in the range 10^{-9} to 10^{-8} $mm^3(Nm)^{-1}$ [137]. The thin lubricating graphitic film on top of the hard supporting ta-C layer thus provides an ideal system to reduce friction and wear.

The surface acoustic wave (SAW) analysis showed that the elastic modulus of ta-C coatings was reduced about 5% due to sliding action against the Al_2O_3 pin [69,70]. In addition, the phase contrast imaging atomic force microscopy (AFM) showed a lower elasticity of wear surface compared to the original film. The thickness of this surface layer was the greatest at the asperity summits, where the local contact pressure was high and the temperature flash was

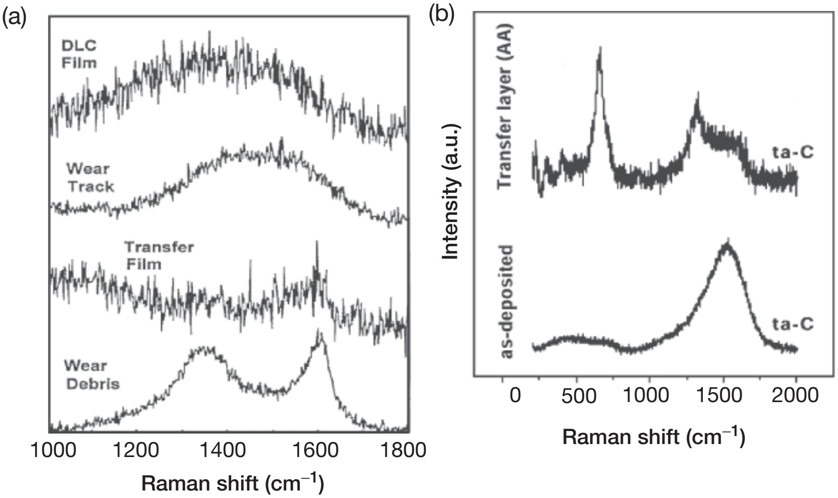

Fig. 15 (a) Comparison of Raman spectra recorded for as deposited hydrogen-free DLC film, wear track, wear debris and transfer film formed after 10^5 sliding cycles in pin-on-disc test in ambient air (50% RH). (From [137]). (b) Raman spectra of hydrogen-free ta-C film as deposited and the transfer layer generated in ambient air (30–40% RH). (After [124].)

most probable [1]. These phenomena can be related to the tribochemical changes occurring on the film surface during sliding action.

Sánchez-López and co-authors carried out Raman analyses on the samples of hydrogenated and hydrogen-free DLC films tested in ambient humid air (30–40% RH), dry air (RH <1%) and dry nitrogen (RH <1%). They detected the presence of a broad peek centred at 650–670 cm^{-1} in the transfer layer (Fig. 15). The presence of these peaks were more evident in the less-hydrogenated a-C:H or hydrogen-free ta-C coatings tested in ambient air. The peaks were attributed to the formation of iron oxide by tribochemical reaction of the uncoated steel ball in ambient air [124].

The ta-C films typically can have a high surface roughness, which increases friction in the beginning of sliding. This effect of surface roughness can be reduced by optimizing the process parameters favouring smoother surfaces [58]. Moreover, filtering of macroparticles can be used to reduce their effect in the vacuum arc deposition [46]. The steady-state friction values for the ta-C films deposited by filtered arc deposition have been measured in the range 0.08 [125].

The hydrogen-free amorphous carbon (a-C) films have similar friction performance to ta-C coatings showing reasonably low friction in humid environment. Friction coefficient values of 0.2 have been measured for the pure a-C film in sliding tests carried out in ambient air against steel with wear rate of 0.06×10^{-6} mm^3(Nm)$^{-1}$. The friction evolution of pure a-C film shows typically a fluctuating trend, and therefore a-C films are in most cases doped with metallic species, like Cr and W. The metal-doped a-C films have typically lower and smoother evolution of friction compared to undoped a-C films.

The metal doping, on the other hand, increases the wear rate of the films compared to undoped ones as shown in Fig. 16 [102]. The Cr-doped films had a stable friction performance around 0.1–0.2 and the wear rate of 10^{-6} $mm^3(Nm)^{-1}$, when sliding against Ti and Al counterparts in humid air studied by Konca et al. [65,66]. Against WC counter material, friction coefficient values of 0.07–0.05 and wear rates of 0.043 × 10^{-6} mm^3 $(Nm)^{-1}$ to 0.021 × 10^{-6} mm^3 $(Nm)^{-1}$ were measured in ambient air as the load was increased from 40N to 80N [31].

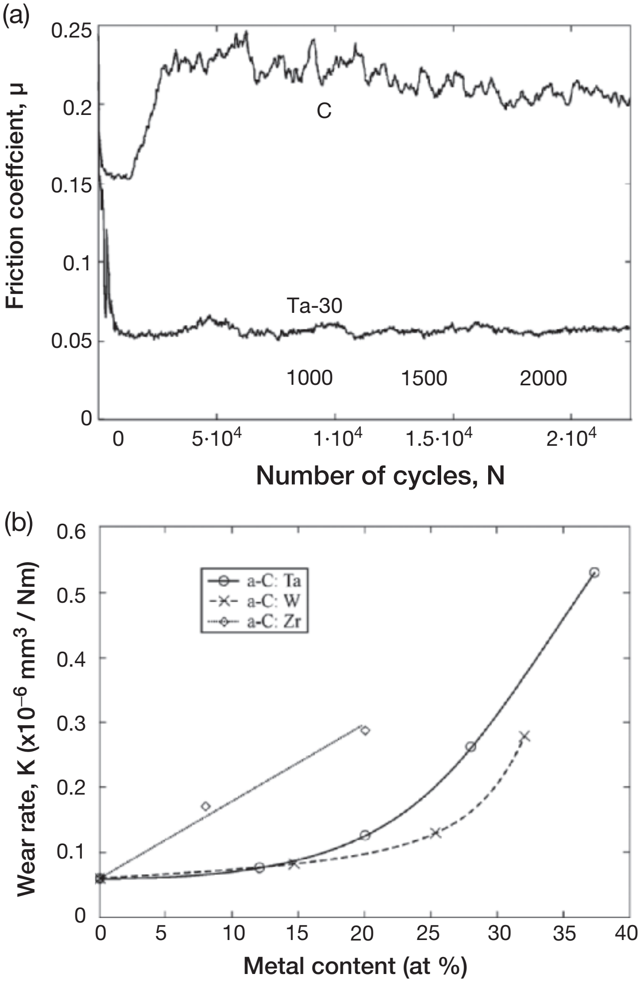

Fig. 16 (a) The friction performance of the pure a-C and Ta-doped a-C films and (b) the wear rates of a-C coatings doped with different metals from pin-on-disc tests. (After [102].)

The low friction performance of hydrogen-free DLC films in ambient air can be attributed to the presence of humidity. The H_2O molecules are adsorbed on the DLC film surface terminating the dangling bonds of the DLC film. By this mechanism the bond strength between the interacting surfaces is reduced to about 0.21 eV per bond, typical for the hydrogen bonding of water molecules at C=O sites [39], providing reasonable low friction performance. On the other hand, the a-C films are sp^2 bonded and a sp^2-bonded graphitic transfer layer is also formed on the contact surface of ta-C films. In humid conditions, these graphitic carbon species can assist in providing low friction performance.

3.4 The Friction and Wear Performance of Hydrogen-free DLC Films in Vacuum and Dry Environments

The hydrogen-free DLC coatings have a different behaviour in inert environments, compared to hydrogenated DLC films, since they represent high friction and wear performance in vacuum and in dry environment. For the ta-C coatings prepared by PLD technique the friction was increased from about 0.08 to 0.5 after several thousand sliding cycles in vacuum (10^{-7} Pa), as observed by Voevodin and co-workers (Fig. 17). The authors discovered surface graphitization to be responsible for the low friction in humid air, and high friction in vacuum for the hydrogen-free DLC coatings [135,137,139]. Meunier et al. [91] measured in vacuum (10^{-3} Pa) similar high friction values 0.5–0.7 for the ta-C films deposited by filtered cathodic arc. The friction behaviour is typically erratic in vacuum, but in ambient atmosphere steady friction is typically detected. In vacuum conditions the friction coefficient has also been observed to increase as the normal force is increased [2].

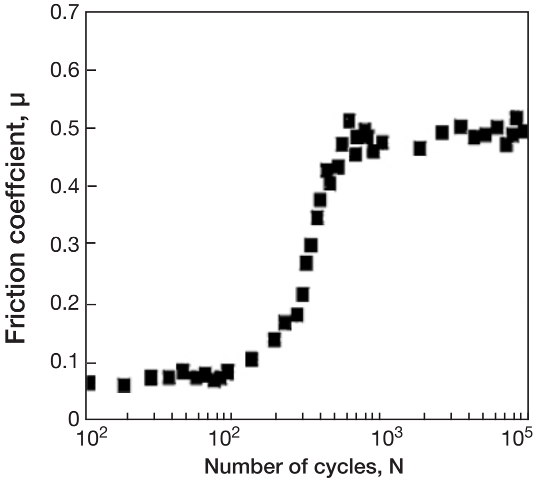

Fig. 17 The friction coefficient evolution for hydrogen-free DLC (ta-C) film sliding against sapphire ball in high vacuum conditions (10^{-7} Pa). (After [137].)

The influence of humidity on the friction performance of the vacuum arc-deposited ta-C coatings was studied by [3]. The ta-C coated steel balls were tested against the ta-C coated discs by pin-on-disc experiments conducted in a vacuum chamber. The tests were carried out under vacuum (10^{-6} Pa), as well as in an atmosphere of hydrogen, oxygen and water (1,300 Pa corresponding to 50% RH). In vacuum, ta-C coating performed high friction in the range 0.65 accompanied with high wear. After introduction of oxygen, hydrogen and water vapour into the chamber, the friction was reduced to approximately 0.25, 0.15 and 0.07, respectively, with a reduced wear of the coating. The ta-C coatings thus have a different friction performance in vacuum compared to a-C:H, but similar frictional response in humid environments close to the water condensation pressure as observed in the Fig. 18. Similar friction performance was also observed by [62].

The ta-C coatings deposited by pulsed vacuum arc technique, exhibited high friction coefficient values in dry nitrogen and dry air, when ta-C coated discs were slid against steel balls with low sliding speed. The friction values were in the range 0.6 in dry air and in the range 0.6–0.8 in dry nitrogen as presented in Fig. 19 [121]. However, the friction of the ta-C coating could be reduced when the ta-C coatings were doped with hydrogen by depositing the films with pulsed vacuum arc discharge in hydrogen (H_2) or methane (CH_4) atmospheres. The friction coefficient was decreased from 0.7 to 0.28 as the hydrogen content of the film increased from >1 at. % to 16 at. % hydrogen as shown in Fig. 20 [71]. The results clearly show the importance of the presence of water

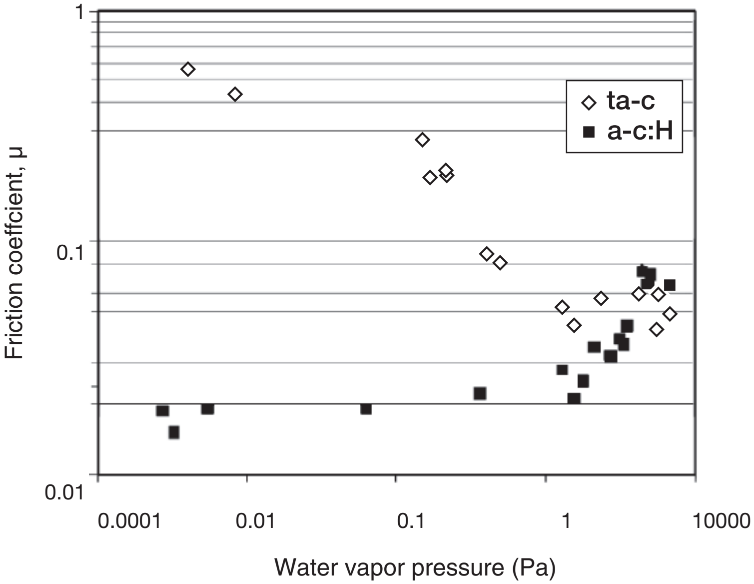

Fig. 18 Friction performance of hydrogen-free ta-C and hydrogenated a-C:H as a function of water vapour pressure. (After [4].)

vapour in the surrounding environment or presence of hydrogen in the coating in order to reach low friction performance of ta-C coatings.

The hydrogen-free amorphous carbon (a-C) films, deposited by magnetron sputtering technique, have similar high friction performance in dry and inert atmospheres to ta-C films. In argon, the a-C films have a friction coefficient of 0.63 against Al (K = 1.28 × 10^{-5} mm^3/m), 0.53 against Ti (K = 1.39 × 10^{-4} mm^3/m) and

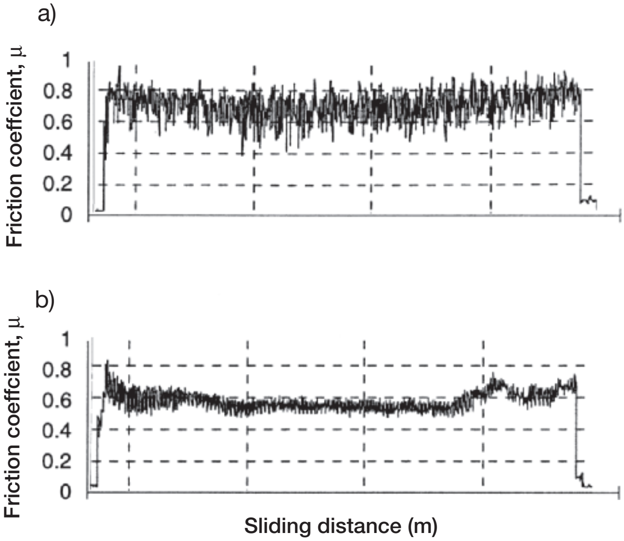

Fig. 19 The friction coefficient of ta-C coating sliding against steel pin (AISI 52100) in (a) dry nitrogen and (b) dry air. The normal force was 5 N, sliding velocity 0.02 ms^{-1} and sliding distance 24 m. (After [119].)

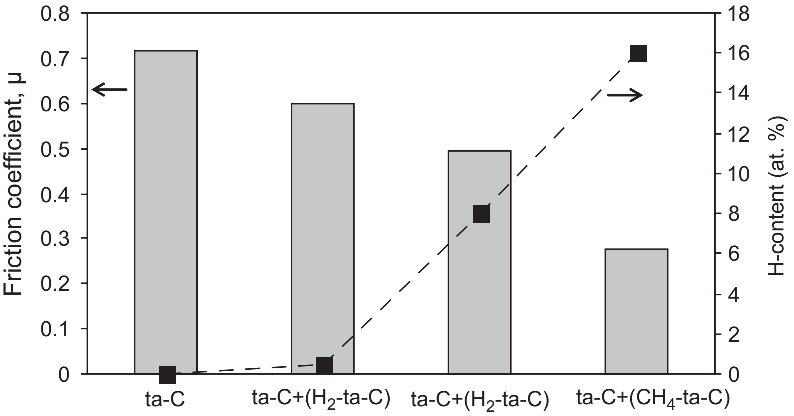

Fig. 20 The coefficient of friction for ta-C coatings with different hydrogen contents. The pin-on-disc tests were carried out with steel pins (AISI 52100) with 5 N normal force and sliding velocity of 0.02 ms^{-1} in dry synthetic air (about 0% RH). (After [121].)

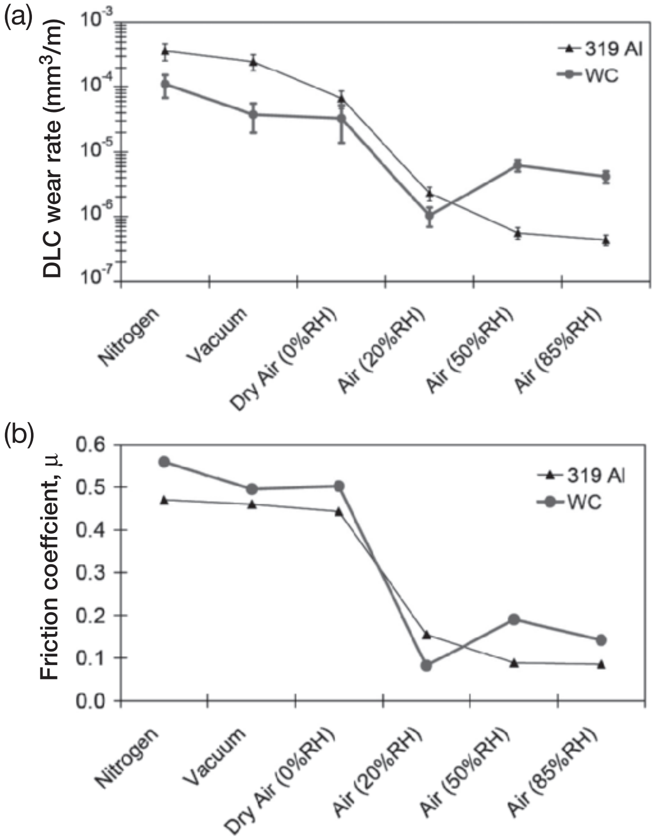

Fig. 21 (a) The wear rates and (b) the steady-state friction coefficient values of the hydrogen-free a-C coatings against Al and WC under various test environments. The normal force was 4.9 N and the sliding velocity 0.12 ms^{-1}. (After [64].)

0.48 against Cu (K = 1 × 10^{-9} mm^3/m). In humid air (22% RH) the friction coefficient values are considerably lower, against Al 0.18 (K = 7.87 × 10^{-7} mm^3/m), against Ti 0.09 (K = 7.34 × 10^{-7} mm^3/m) and against Cu 0.39 (K = 7.99 × 10^{-7} mm^3/m)$^{-1}$ [65,66].

In addition, the Cr doped a-C coatings had a high friction in vacuum, nitrogen and dry air (5% RH) as shown in Fig. 21. In humid air, the friction decreases as the humidity increased from 20% to 85% RH [64]. In hydrogen environment the friction coefficient is about 0.015 and a carbonous transfer layer is detected on the wear surface [109].

The importance of humidity for the low friction performance of hydrogen-free DLC films is evident from the experimental results. In ambient, humid air, low friction performance can be achieved for the ta-C and a-C coatings, but in vacuum and in dry environments high friction coefficient values combined with high wear have been observed. The friction performance of hydrogen-free ta-C films is influenced by the highly sp^3-bonded hydrogen-free structure of the film. The surface carbon atoms of the ta-C are bonded to their neighbouring atoms with three σ-bonds, leaving the fourth bond free, dangling out of the surface. In open air these dangling bonds are terminated by adsorbates, like e.g. water molecules or hydrogen. In inert gas or in vacuum, the adsorbed atomic species will be removed due to mechanical action of thermal desorption. If the σ-bonds are exposed, the dangling bonds can establish strong covalent interactions with the atoms of the counterface material causing high adhesion between the surfaces indicated by high friction [4,19].

The AFM-based nanowear tests have shown that the a-C films deposited by DC magnetron sputtering, are covered with thin (1.5–2.0 nm) graphite-like surface layers [80]. Moreover, for ta-C coatings the surface atoms are found to reconstruct into sp^2 sites often bonded in graphitic rings. This reconstruction, by placing the dangling bonds on adjacent surface atoms lower the energy by π-bonding and creates lower surface energy [7]. Earlier, also McKenzie et al. [87] have detected the sp^2-enriched surface of ta-C coating. These results suggest that both the types of hydrogen-free DLC films have sp^2-bonded carbon structure at the surface. The phenomenon is enhanced by the graphitization taking place due to tribological action. This suggests that the friction performance of hydrogen-free DLC films is influenced by the graphitic nature of the film surface and the graphitic nature of the generated transfer layer. The graphitic species require contaminants, like water molecules or hydrocarbons, to be present in the tribocontact in order to provide low friction performance [55]. Since the water molecules and hydrocarbon species fairly readily desorb from the surface due to sliding action, the friction of hydrogen-free DLC films increases in dry and inert environments.

4 Thermal Effects on Tribological Performance of DLC Coatings

The performance of the DLC films at elevated temperatures is greatly influenced by the nature and structure of the films. The hydrogen and water vapour also play a key role in the high temperature performance of the DLC films. The dehydrogenation of the a-C:H film structure will change the coating structure and thus the performance of the coatings. On the other hand, for the hydrogen-free DLC films the desorption of water vapour is detrimental for the friction and wear performance at elevated temperatures.

4.1 The Thermal Effects on Hydrogenated DLC Films

The thermal stability of DLC films differ according to the film structure and composition. In the hydrogenated DLC films, the hydrogen plays an important role in the bonding configuration by stabilizing the tetrahedral coordination (sp^3

bond) and thus controlling the film properties. The existence of hydrogen in DLC film increases the proportion of sp^3 bonds. Annealing the hydrogenated DLC film at elevated temperatures causes hydrogen desorption in the film. Hydrogen effusion will occur in a-C:H films at elevated temperatures from 300°C to 600°C depending on the deposition parameters used for the coating deposition [141].

The polymeric DLC films will have lower hydrogen effusion temperature in the range 260–350°C compared to the harder films (deposited at higher bias voltage) in the range 550°C. The dense ta-C:H coatings have an even higher annealing temperature in the range 700°C. The conversion of film structure to nanocrystalline graphite can also start at lower temperature for polymer like films, in the range 300°C, when heated in air [112,130]. Gao and co-workers reported the heating of hydrogenated DLC structure up to temperature 420 K (147°C) to cause substantial amount of hydrogen desorption from the surface, detected by mass spectroscopy. This effect was accompanied with an increase in friction and wear [38]. According to Liu et al. [86], the structure of a-C:H showed no appreciable change after annealing up to 400°C, but at higher temperatures the dehydrogenation of the a-C:H structure occurred followed by precipitation of small graphite crystals. However, the hardness remained approximately constant after annealing at the temperature range 200–700°C.

Miyoshi et al. [97] reported thermal stability to higher temperatures, since the increase in friction was observed when the annealing temperature raised from 500°C to 600°C and remained high in the range 600–700°C. Memming et al. [89] observed the loss of hydrogen in DLC films when annealed above 550°C with strong increase in friction up to 0.68 in UHV and dry nitrogen. However, no significant change was observed in humid atmosphere. Similar effect has been observed by Grill [42].

The general trend at elevated temperatures is the increased wear [23,81, 132]. The evolution of hydrogen is followed by the phase transformation of sp^3 to sp^2 bond structure. The graphitization as well as oxidation of the hydrogenated DLC film will wear out the DLC structure rapidly at elevated temperatures. Erdemir and Donnet [22] reported an increasing wear rate for DLC at elevated temperatures from 100°C as observed in Fig. 22. Compared to the room temperature tests (0.000186×10^{-6} mm^3 $(Nm)^{-1}$) the wear rate increased dramatically for the a-C:H film in 250°C (1.39×10^{-6} $mm^3(Nm)^{-1}$). Liu et al. [81] reported a rather stable wear performance of a-C:H films sliding against Al_2O_3 in humid air at elevated temperatures up to 200°C, but in 300°C and above, the wear increased dramatically leading to total rupture of the coating due to graphitization. However, the friction was decreased from 0.15 down to 0.02 with increasing temperature, but the wear life of the film was short at high temperatures (Fig. 23).

When testing the annealed films in room temperature unchanged wear resistance for hydrogenated DLC films was detected up to an annealing temperature of 300°C [77,78] and 400°C [133]. It was also shown that the testing environment had a greater effect on wear performance compared to the annealing effect. Grill

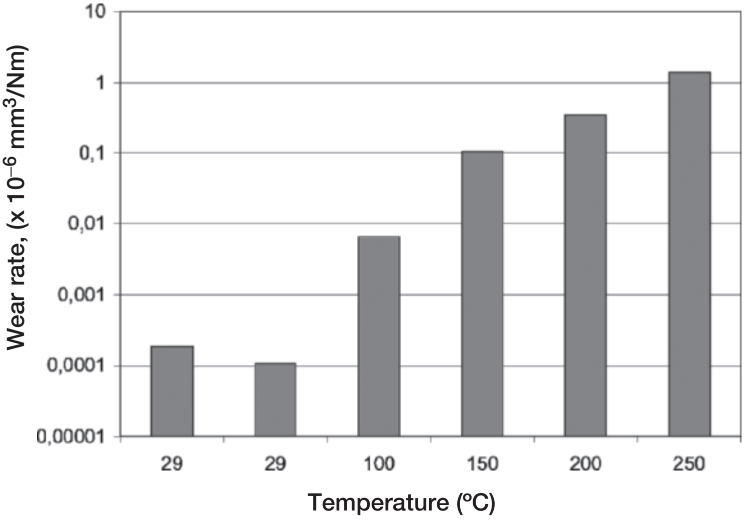

Fig. 22 Effect of temperature on wear performance of hydrogenated DLC film. (After [22].)

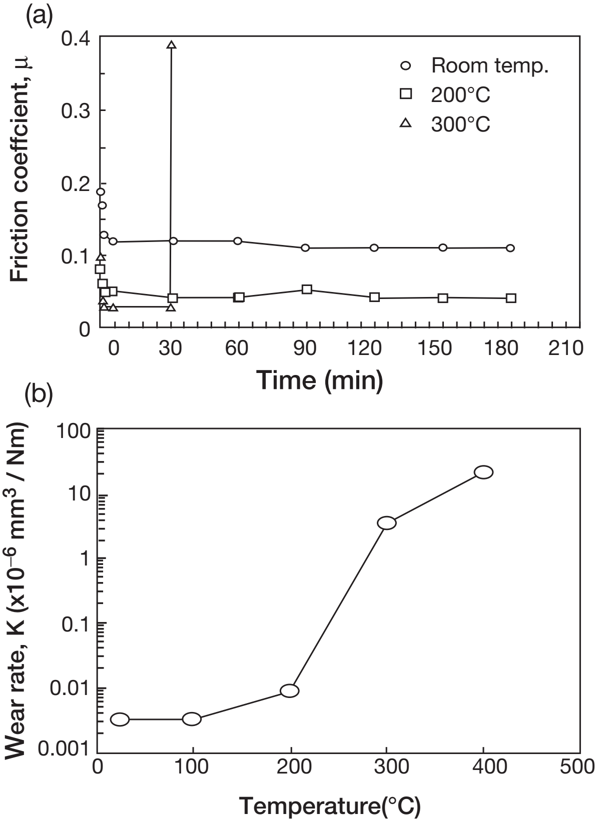

Fig. 23 (a) The friction coefficient evolution of DLC films sliding against Al_2O_3 at different temperatures. (b) The influence of temperature on wear rates of the hydrogenated DLC film. (After [81].)

et al. [47] have reported that the films deposited in higher temperature and with higher bias voltage are more stable at elevated temperatures and they remained wear-resistant even after annealing at a temperature of 590°C.

The thermal stability of a-C:H films can be enhanced by doping, e.g. with Si. The increased silicon content has been observed to stabilize the structure and the Si-doped film graphitize in a higher temperature compared to pure a-C:H. The integrated intensity ratio I_D/I_G of the Raman shift describing the change in the bonding structure was increased to 400°C for the Si-doped DLC compared to 300°C for the pure DLC. Only insignificant oxidation occurred for the Si-doped a-C:H films at 300°C and the remaining carbon was converted to the graphitic phase at 600°C compared to 500°C for the undoped DLC [142]. On the other hand, other doping species, like fluorine, were found to decrease the temperature stability [99].

4.2 Thermal Effects on Hydrogen-free DLC Films

The hydrogen-free DLC films resist oxidation or phase transformations to much higher temperatures compared to hydrogenated DLC films. The tetrahedral amorphous carbon ta-C contains hydrogen only as an impurity and the structure is a highly sp^3 hybridized. Due to their structure the ta-C films deposited by vacuum arc discharge are stable up to 1,000 K (727°C) when annealed in vacuum [87]. If heated in air, oxidation of the film is observed at 450–500°C [112]. However, annealing at 400°C (673 K) has been reported to influence the wear performance of ta-C by increasing the wear rate to some extent when sliding against stainless steel after the process [74].

Concerning the ta-C films deposited by pulsed laser ablation technique, the thermal stability has been shown to be related to the initial structure (sp^3/sp^2 ratio) and chemical properties of the coating. Changes in sp^3/sp^2 bonding ratio of the coating has been reported to occur at annealing in 300°C [59]. However, good thermal stability has been reported up to 900 K (627°C) in UHV for optimized coatings [119].

In cryogenic temperatures, the friction of ta-C coating was increased to values 0.3–0.6 in 77 K (−204°C) from the those measured against steel counterface in room temperature (about 0.2). The lowest friction coefficient (about 0.2) in 77 K was measured for the ta-C against ta-C sliding pair with a lower intrinsic hardness of the coating (40 GPa). Smoothening type of wear was observed for the ta-C coating in low temperatures [106].

The hydrogen-free amorphous carbon (a-C) films deposited by magnetron sputtering are reported to be thermally stable up to 300°C, after which the hardness drops drastically with temperature due to graphitization of the coating structure. The thermal stability can, however, be improved by using, e.g. nanocomposite structures [147]. The high temperature pin-on-disc tribometre tests with a-C coatings showed increased wear at temperature as low as 120°C due to loss of stability

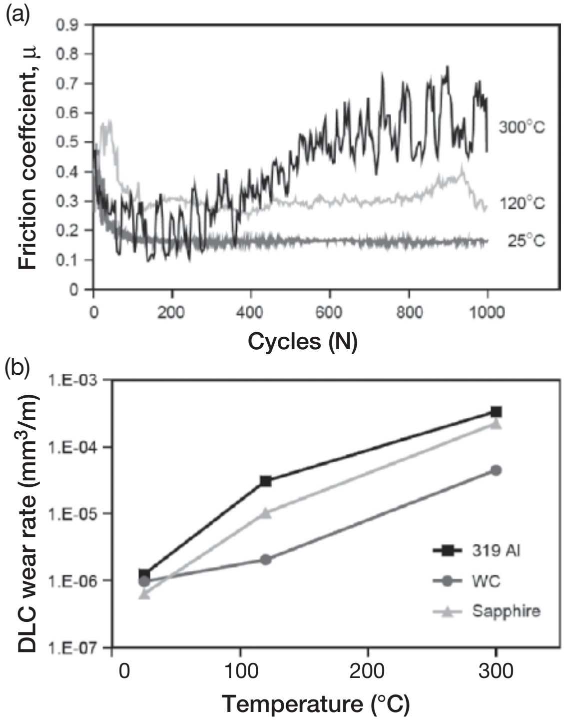

Fig. 24 (a) The friction coefficient of a-C coated discs and 319 Al pins sliding at temperatures 25°C, 120°C and 300°C. Tests were run for 60 m with a normal load of 4.9 N and sliding velocity of 0.12 ms^{-1}. (b) The variation of the wear rate of a-C coating with temperature when tested against 319 Al, WC and sapphire at temperatures 25°C, 120°C and 300°C. Test was run for 1,500 m at 25°C and for 69 m at 120°C and 300°C using 4.9 N applied load. (After [66].)

and significant oxidation of the coating in air at elevated temperatures. The wear of a-C coatings is increased dramatically when tested at elevated temperatures accompanied with the increase in friction as shown in Fig. 24 [66]. The increased friction performance is attributed to the absence of adsorbed water in the tribocontact, which is necessary for the low friction performance of the hydrogen-free coatings.

5 Concluding Remarks

The friction and wear performance of DLC films varies in different environments and according to changes in surrounding humidity. The friction performance and different mechanisms controlling the tribological interaction are represented schematically in Fig. 25.

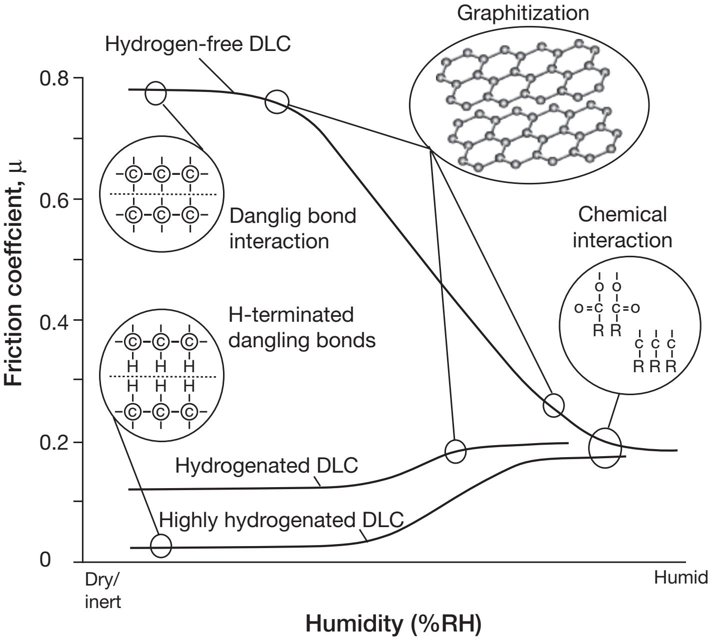

Fig. 25 Schematic picture of friction performance of DLC films as function of humidity and mechanics controlling the tribological performance

In dry and inert environments the amount of hydrogen in the coating structure determines the tribological performance of the DLC coating. The hydrogen-free DLC coatings experience high friction and wear in dry and inert environments. In inert environments the highly sp^3-bonded structure of hydrogen-free DLC film can partly explain the high friction performance. The surface carbon atoms of ta-C film are bonded to their neighbouring atoms with three σ-bonds, leaving the fourth bond free, dangling out of the surface. In ambient humid air, the dangling bonds are terminated or passivated by adsorbates, like water molecules, oxygen or hydrogen.

However, in a dry environment the adsorbates will be removed during sliding due to mechanical rubbing action or due to thermal effects leading to exposed σ-bonds establishing strong covalent interactions with the atoms of the counterface material. This causes high adhesion between the surfaces indicated by high friction. On the other hand, the outermost surface structure of the ta-C films as well as the a-C films has been reported to have a sp^2-hybridized structure. In addition, the graphitization of the hydrogen-free DLC structure has been observed to occur. The graphitic species on the coating surface can thus also contribute to high friction performance in dry environment, since graphite requires adsorbed water to provide easy shear between the densely packed atom sheets.

The highly hydrogenated DLC films exhibit superlow friction performance in dry and inert atmospheres. The tribological performance of highly hydrogenated DLC films in dry or inert environment is controlled by the interaction between hydrogen-terminated DLC structures or between hydrogen-terminated DLC structure and the transfer layer. The DLC surface with hydrogen-terminated dangling bonds experiences weak bond strength of about 0.08 eV per bond, typical for van der Waals bonding of hydrocarbons [39]. Besides high hydrogen content, great smoothness of the surface is an essential requirement for the contacting surfaces to reach the superlow friction level.

The hydrogenated DLC films that have a moderate amount of hydrogen in their structure can have a superlow friction coefficient in an inert or dry environment, but only for a limited period of time. The friction of such DLC films tends to increase to higher values, even close to values experienced by hydrogen-free DLC films after longer period of sliding in dry environment. This phenomenon occurs due to removal of hydrogen from the surface due to sliding action causing increased interaction of dangling bonds of contacting surfaces. However, this increased friction coefficient can be reduced to superlow level if hydrogen is provided from the environment. The depleted hydrogen on the surface also leads to graphitization of the outermost surface of the hydrogenated DLC structure, thus increasing the friction in dry environment. These phenomena verify the hydrogen-controlled tribological mechanism of hydrogenated DLC films acting in dry and inert environments.

The superlow friction performance of hydrogenated DLC films is destroyed in humid air due to adsorbed water vapour on the contacting surfaces leading the higher friction values. On the contrary the friction of hydrogen-free DLC films is reduced in humid air from the high values experienced in dry environment, due to dissociation and adsorbtion of water molecules on the DLC film surface and formation of C–OOH and C–H bonds that can passivate the dangling bonds of the coating surface. As the humidity is increased the friction performance of both hydrogenated and hydrogen-free DLC films will converge showing similar low friction coefficient in humid environment.

The friction values of DLC films vary generally in the range 0.1–0.2 when humidity and oxygen is present in the surrounding environment. In this case the tribological interaction is controlled by water vapour and gas adsorption on the contacting surfaces. Oxidation of the DLC film and the counter material will also occur in oxygen containing environments accompanied with the wear of the counterpart showing the importance of tribochemistry in humid environments. The wear resistance in humid environment is related to the hardness of the film and in most cases the hard hydrogen-free ta-C films exhibit the best wear performance.

In order to further understand the tribochemical reactions acting in the tribological contacts of DLC films, advanced analyses techniques, like phase contrast imaging AFM, XPS, EDS, Auger and Raman, are required for the study of friction- and wear-induced phenomena. It is also necessary to combine the knowledge of tribology, physics and chemistry in order to fully understand the controlling mechanisms of DLC films in tribological contacts.

The elevated temperatures tend to disturb the tribological performance of DLC films. The hydrogenated DLC films experience hydrogen effusion in elevated temperatures accompanied with graphitization of the film structure leading to increased wear with increased temperature. The hydrogen-free ta-C films have a more stable structure in high temperatures, but the friction is increased at elevated temperatures due to removal of water vapour from the surface. Thus high temperature has a similar effect on tribological performance of ta-C films compared to dry environment.

The dependence of the tribological performance of DLC films on the surrounding environment and the temperature, directs the use of the films in different applications. The hydrogen-free DLC films cannot be used in dry or inert atmosphere, since they require humidity for low friction performance. The hydrogenated DLC films, on the other hand, are sensitive to elevated temperatures causing degradation of the film performance. In normal atmosphere, both hydrogenated and hydrogen-free coatings have similar friction performance but the wear resistance is dependent on the film structure, the hydrogen-free ta-C film providing best wear resistance in normal atmosphere. These phenomena among other things need to be considered when DLC coatings are used in practical applications.

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