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MoDTC lubrication of DLC-involving contacts. Impact of MoDTC degradation

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ABSTRACT: Recently Diamond-Like Carbon (DLC) coatings have attracted considerable attention due to their low friction, high hardness, good wear and corrosion resistance, high thermal and chemical stability. Although considerable research has been conducted on the effect of molybdenum-based additive, e.g. molybdenum dithiocarbamate (MoDTC), on the boundary lubrication of DLC coatings, the wear mechanisms leading to the coating removal are not fully understood to date. Moreover, the impact of degradation of MoDTC-containing base oil on the tribological properties of DLC coatings has not been investigated. This study could help to elucidate the mechanisms by which the coating is worn out in presence of MoDTC-containing base oil.

In this work, the friction and wear performances of different types of DLC coatings with different hydrogen contents and doping elements have been investigated in presence of MoDTC-containing base oil. To enable the correlation between these changes and the modification of contact surface chemistry, tribofilms generated during friction were investigated by SEM combined with Energy Dispersive X-ray Spectrometry (EDX) and X-ray Photoelectron Spectroscopy (XPS). A new mechanism explaining the severe wear experienced by DLC coatings when lubricated with a MoDTC-containing base oil is proposed.

1. Introduction

To improve the lubrication performance of modern engine lubricants, a complex additive package is blended to the base oil. One of the key group additives is the friction modifier, employed to lower the friction coefficient between two rubbing surfaces. One of the most used among them is molybdenum dithiocarbamate (MoDTC) [1,2].

In the past decade, Diamond-Like Carbon (DLC) coatings have been applied for automotive applications as surface protective layers due to the outstanding mechanical and tribological properties, such as high hardness, low friction and superior wear resistance [3,4]. Recent studies have shown that, despite the friction reduction obtained, the interaction between MoDTC and DLC coating often leads to a high wear rate [5,6,10]. Kosarieh et al. [10], for example, correlate the high wear of DLC to the molybdenum-containing products decomposed from MoDTC. They found that DLC wear depends on the MoDTC concentration in the lubricant and that the addition of ZDDP additive could mitigate this wear. An abrasive wear mechanism for DLC material when lubricated with oil containing MoDTC friction modifier was proposed by Shinyoshi et al. [5] and confirmed by Haque et al. [6]. In these studies it has been hypothesized there is an interaction between the DLC coating and the MoO_3 particles, derived from MoDTC decomposition [7,8]. However other authors [9] have demonstrated that there is no direct correlation between the DLC wear and MoO_3 concentration. Further investigations [11,12] have shown the hybridization change of carbon from sp^3 to sp^2-bonding due to high temperature, pressure and mechanical stresses in the contact can play a role in the wear of DLC material. It was proposed that the hybridization change increases the sp^2-content on the top of the DLC structure, leading to the delamination of this soft, amorphous carbon layer [12]. Although all these studies showed that DLC material suffers strong wear when it is lubricated with the MoDTC-containing lubricant, it remains, unclear what the mechanism of wear is.

The aim of this work is an accurate investigation of surface chemical modification undergone by lubricated DLC coatings in the presence of MoDTC additive. In order to address the question of the strong wear of DLC materials, five different coatings, varying by hydrogen content, hardness and presence or absence of doping agents (silicon), were selected. To develop a further understanding on the interaction between DLC and MoDTC additive, the effect of lubricant degradation on the DLC/steel contact has been investigated. Special attention was paid to two DLCs, which showed completely different tribological behaviours. Chemical analyses have been performed on the tribofilms formed on the contact surfaces to obtain more information about the severe wear that can occur on some DLC coatings. Based on these experimental and analytical results, a new wear mechanism has been proposed.

2. Materials and Methods

2.1 DLC COATING AND LUBRICANTS

Five different types of DLC coating supplied by Oerlikon Balzers France were tested in this work. The main properties of these coatings are given in table 1.

DLC type	DLC detailed name	Short name	H [%]	Si [%]	Average top layer DLC Thickness [µm] (total thickness)	Nano-indentation Hardness [GPa]	Deposition technique
a-C:H	a-C:H process 1	a-C:H	-	-	2.0 (3.5)	21	PACVD
a-C:H	High hydrogen a-C:H Process 2	HHS	33	-	0.9 (1.9)	22	PACVD
a-C:H	Low hydrogen a-C:H Process 2	LHS	29	-	1.5 (2.3)	20	PACVD
ta-C:H	Hard ta-C:H	ta-C:H	30	-	1.3 (3.0)	38	PACVD
a-C:H:Si:O	DLC doped with Si & O /a-C:H process 2	Si-doped	34	14	1.2 (2.3)	18	PACVD

Table. 1. Main characteristics of DLC coatings used in this work. (H& Si content measured by ERDA/RBS).

Substrates are standard 100C6 steel with a known composition based on ISO 683-17:2014 (Table 2), with a roughness of about Ra=0.05 µm.

All substrates before deposition are cleaned into an industrial water based cleaning line, rinsed in high quality DI wter and dried by hot air at 100°C. Before deposition itself, there is in situ argon sputtering of the top surface (about -0.1 µm) in order to remove the superficial contamination (oxide layer).

	Chemical composition%						
100Cr6	C	Si	Mn	P	S	Cr	Mo
	0.93–1.05	0.15–0.35	0.25–0.45	<0.025	<0.015	1.35–1.60	<0.10

Table. 2. Chemical composition of 100C6 based on the normative ISO 683-17:2014.

2.2 Lubricants

The lubricant used for this study was prepared in standard base oil belonging to group III, supplied by TOTAL Company. Molybdenum dithiocarbamate (MoDTC) additive was added to a concentration of 1 wt% and the mixture was warmed up to 65°C and continually stirred for 10 minutes. A schematic representation of MoDTC structure is shown in Figure 1, where X can be S or O atoms (although mainly S) and R is a mixture of C_8 and C_{13} alkyl chains.

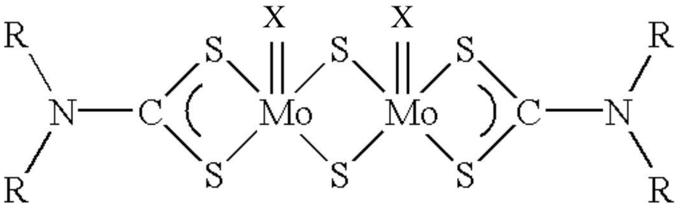


Fig 1. Chemical structure of molybdenum dithiocarbamate (MoDTC).

2.2.1 Degradation procedure

The thermo-oxidative degradation procedure was carried out based on the CEC-L-48-A00 standard , setting the temperature at 160°C under air atmosphere. To simulate the ageing process, a thermos-controlled heater and round-bottom flask containing 300 mL of oil were used. The flask is connected to a condenser to reduce the evaporation losses of the more volatiles components [13]. Four different ageing times have been considered: 0 h (fresh oil), 2 h (at which the oil started to change in colour), 5 h (the formation of solid-like particles was evidenced) and 8 hours (at which the oil became completely dark).

2.3 Tribological experiments

Tribological experiments were performed using a ball-on-flat reciprocating tribometer. The counter specimen is an AISI 52100 steel ball of 6.7 mm radius. Boundary lubrication conditions were achieved using an appropriate combination of load, speed and temperature. The ball is reciprocated for one hour against the DLC-coated flat coupons with an applied load of 8N (maximum initial Hertzian Pressure of 800 MPa), a sliding speed of 50 mm/s and the stroke length is 5 mm. These conditions were selected to compare the results obtained on DLC/steel to those reported in a previous work [13] using a steel/steel contact.

Prior to the tests, both ball and plate specimens were cleaned in an ultrasonic bath using heptane solvent to remove surface contaminants. To check the repeatability of the results, each test was repeated at least three times. The friction coefficient was monitored as a function of the number of cycles. The wear of DLC was obtained by the following method. After the tribotest, the surface profile of the worn surface was measured using interferometry techniques (Bruker contour GTK-1. The software used to analyse the data is Vision64) to obtain the worn volume. The wear coefficient (m^3/Nm) of the DLC was calculated by dividing the averaged worn volume at the wear track (m^3) by the load (N) and the total sliding distance (m).

2.4 Surface analysis

The worn surfaces of the steel balls and DLC-coated coupons were analysed by SEM/EDX and X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition of the rubbed surfaces. Before these analyses the friction specimens were degreased by several immersions in pure *n-heptane* and then left in an ultrasonic bath for 10 minutes to remove the residual oil.

The XPS analyses is performed with a ULVAC-PHI VersaProbe II spectrometer equipped with a monochromatized Al Kα X-ray source (1486.6 eV), using a 50 µm X -ray spot size. The analysis chamber pressure is lower than 10^{-7} Pa. Standardization in binding energy (BE) is achieved by analysing gold standard sample to locate the well-known energy positions of Au4f5/2 and Au4f7/2 at 84.0 and 87.7 eV, respectively. A charge neutralization system using a dual beam is used to limit the charging effect that can occur on insulating materials, such as DLC. An additional correction is performed on all spectra by setting the C1s line peak used as an internal reference at BE = 284.8

eV. First, a survey spectrum covering a range of 1200 eV was performed to identify all the elements present on the rubbed surfaces. Then the individual peaks were acquired with high-resolution energy and considering a smaller BE range of 15-25 eV. These scans are used for the peak-fitting procedure. Special attention was paid to the carbon (C1s), oxygen (O1s), sulphur (S2p), molybdenum (Mo3d) and iron (Fe2p) spectra. The Shirley background was used for the photo-peak fitting, and quantitative analyses were performed using PHI multipack software with the correct sensibility factors [21]. XPS handbook [14] was used for tracking the binding energy of corresponding chemical species.

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) analysis was used to obtain images of surface topography of the wear scar and information about its chemical composition.

3. Results

3.3.1 Visual Inspection of degraded oils

The darkening of the oils suggests the increasing of degradation level (Figure 2). Along the ageing time, it can be observed that the colour changes from light green (fresh MoDTC-containing oil, 0 h aged) to completely black oil after 8 h of degradation [13].

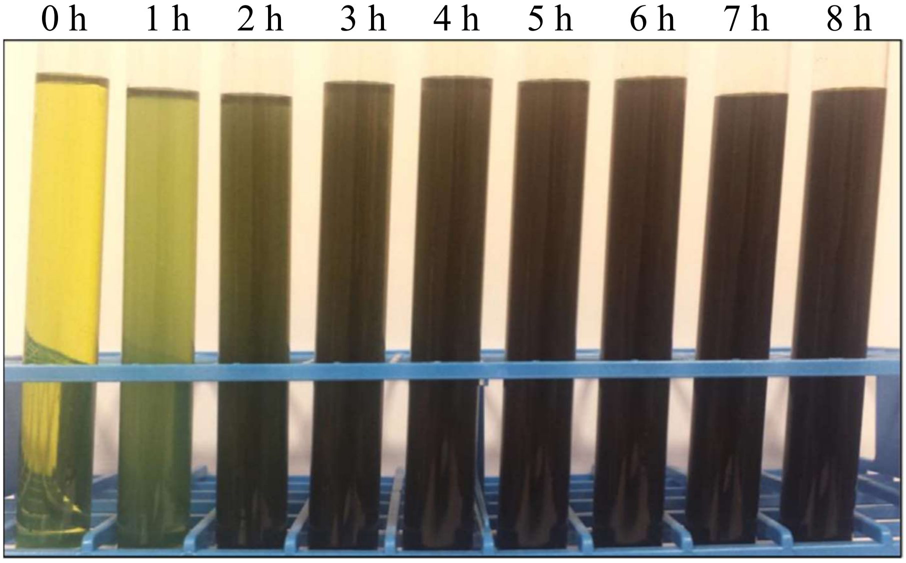


Fig 2. MoDTC-containing base oil colour changes over degradation time.

3.2 Friction and wear performance

The values of steady state friction coefficient (COF) as a function of different DLC coatings for fresh and aged oils are given in Figure 3.

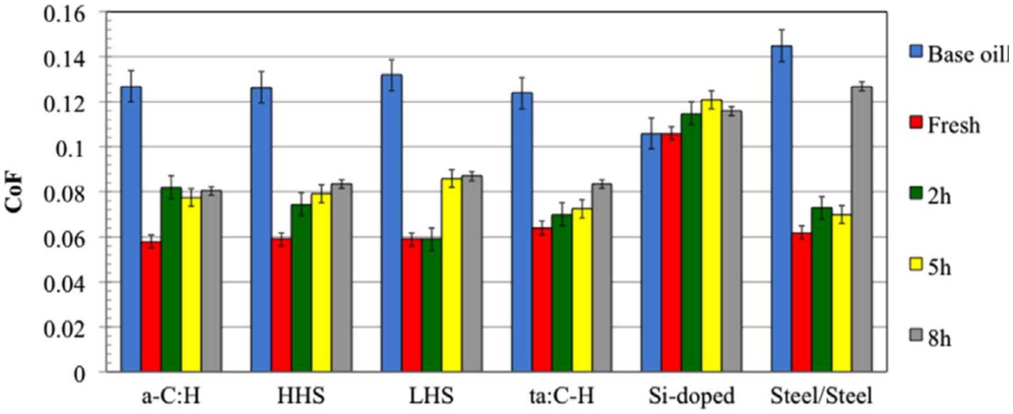


Fig 3. Steady-state friction coefficient for different DLC coatings lubricated with for fresh and aged oils.

All the DLC coatings, except the one doped with silicon and oxygen show the same friction behaviour: the blending of MoDTC into the base oil lowers the friction coefficient until reaching a value similar to that of a steel/steel contact. Moreover, the effect of 5 h aged oil is less significant on steel/steel contact than on DLC contacts. The opposite result is obtained using the oil aged for 8h. The oil degradation process seems to lead to slightly higher friction values, but a significant decrease can still be observed compared with base oil alone for all the DLC coatings except for the DLC doped with silicon and oxygen. This coating is unique in that it gives no friction reduction at all, neither in fresh oil nor the aged one. As are already underlined, the investigations so far indicate that when DLC coated samples are tested in MoDTC-containing oils, it is very important to carry out wear measurements together with friction values [5-8]. Optical images of wear scars on DLC-coated flats are shown in Figure 4. Almost invisible wear was observed for the first four DLCs when employing fresh and low oxidized oil, with only a gradual polishing wear noticeable. The brighter colour of wear track suggests that high-oxidized oils cause higher wear. In the case of steel, a thick tribofilm is formed that can protect the surface. In this case, it is also evident that the antiwear action of the MoDTC additive [17,18] is able to reduce the high wear produced by the base oil.

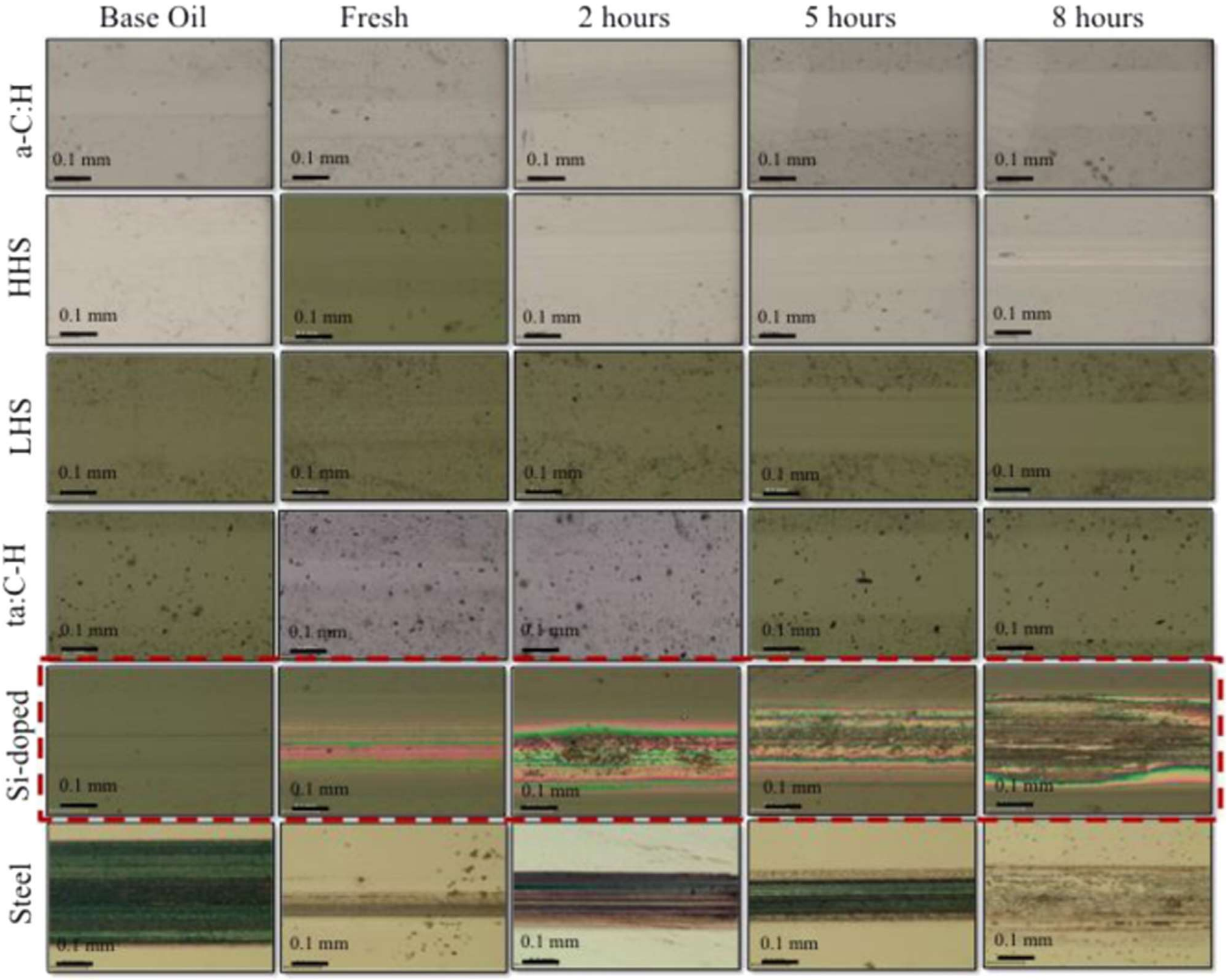


Fig 4. Optical images of wear scars formed on DLC coatings along with degradation time.

Blending MoDTC additive in base oil leads to an extremely high wear for Si-doped DLC. The coating is completely worn out, regardless of the ageing time. The wear rate of DLC-coated flat coupons calculated measured by interferometry is shown in Figure 5. A huge difference in the wear rates can be seen between the Si-doped DLC and the other four coatings, almost more than two orders of magnitude.

To compare the wear data, the wear coefficient related to Si-doped DLC was removed from the graph (Figure 6).

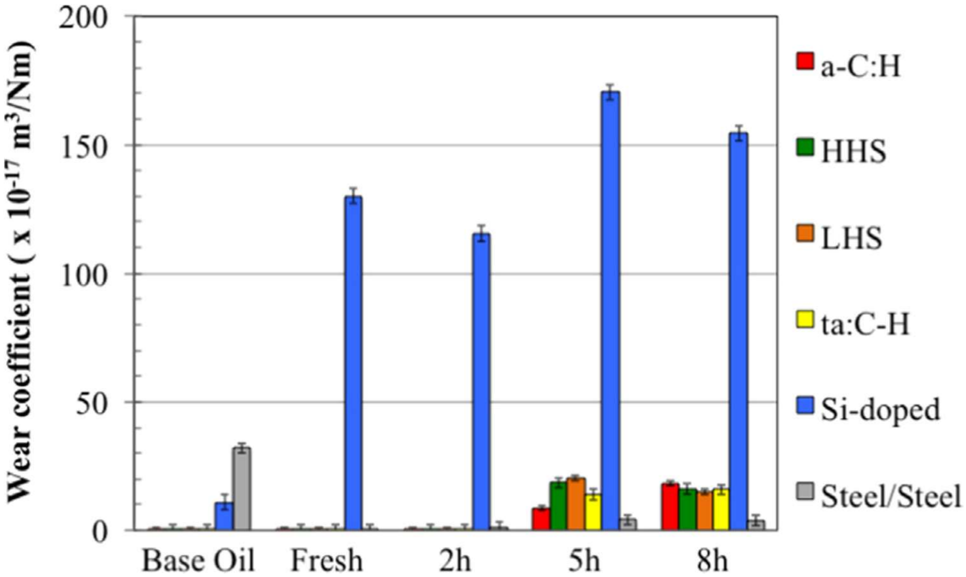


Fig 5. Wear coefficient of DLC flats and steel calculated by means of interferometry.

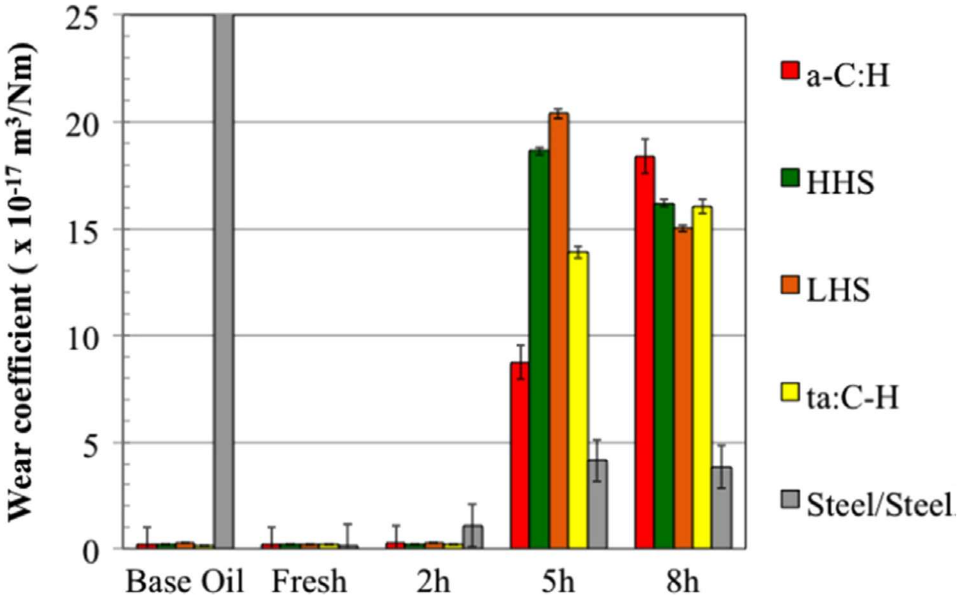


Fig 6. Wear coefficient of DLC flats and steel calculated by means of interferometry without Si-doped DLC.

The results are in good agreement with the wear scar images shown in Figure 4, confirming that the longer the time of oil ageing, the higher the wear coefficient results are. The wear coefficient is also higher compared to that of the steel/steel contact.

Taking into account that the tribological behaviour, friction and wear, of 4 of the DLC coatings seem to follow the same trend, further analyses focus on the two DLCs, i.e. the a-C:H DLC (a promising coating for automotive industry) and the silicon and oxygen doped DLC (with high friction and wear). The comparison between these two DLCs is believed to provide a better understanding of DLC wear mechanisms in the presence of MoDTC additive.

3.3 X-ray photoelectron spectroscopy (XPS)

3.3.1 DLC-coated flat samples

The survey spectra obtained both inside (1) and outside (2) of the wear track on the a-C:H (a) and Si-doped DLC (b) flat coupons after experiments with fresh MoDTC-containing base oil are shown in Figure 7.

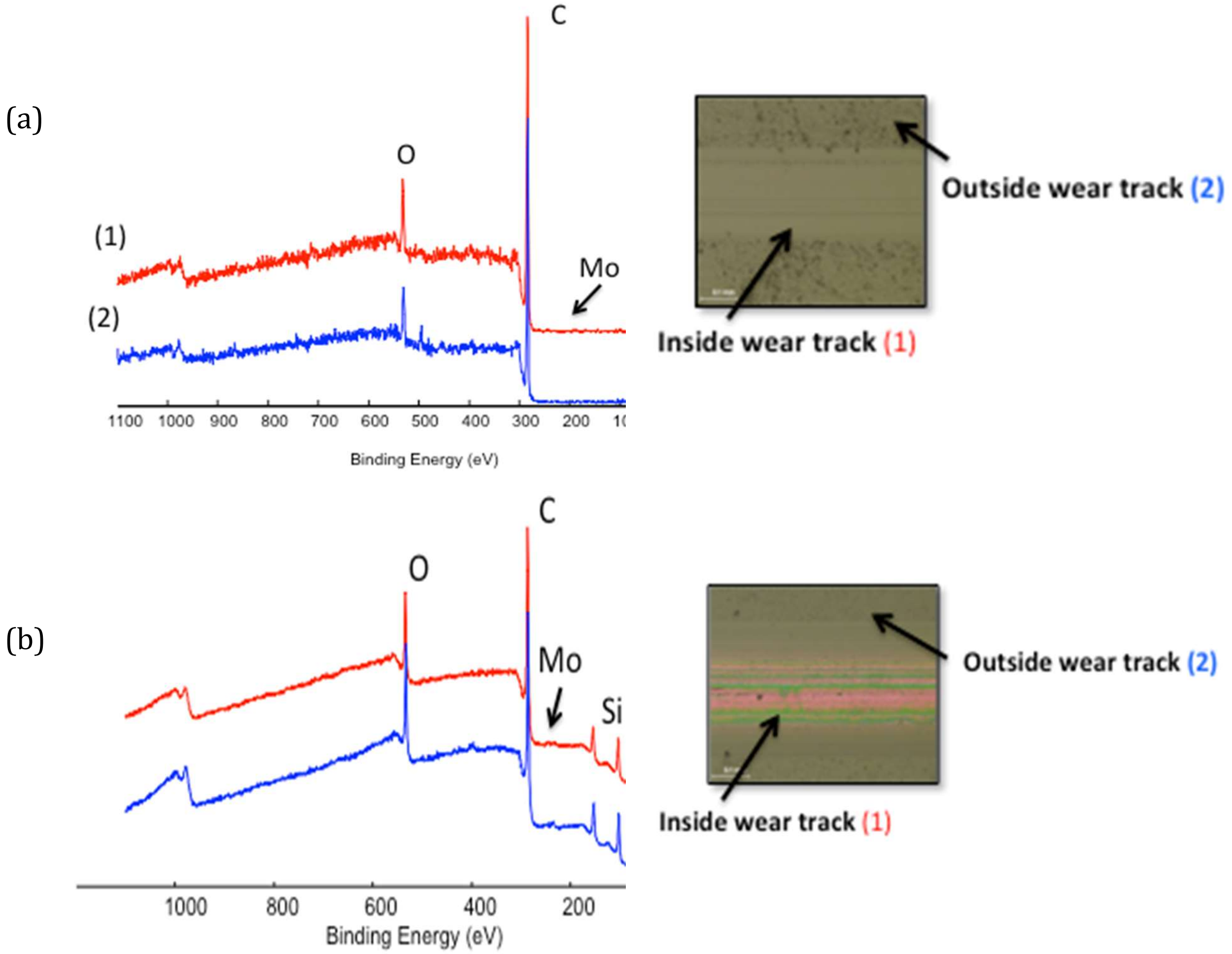


Fig 7. Survey spectra recorded on Hard a-C:H DLC coated flat (a) and silicon-doped DLC (b) lubricated by fresh MoDTC-containing oil.

It is evident that the a-C:H DLC did not show any tribofilm, confirming inertness to MoDTC additive. The same result is obtained for the flat coated with DLC doped with silicon and oxygen. In fact, the amount of molybdenum detected on the coated surface was quite negligible. Therefore, it was decided to perform surfaces analysis on the worn steel counter-ball surface.

3.3.2 Naked steel ball counterpart

The C1s photo-peaks recorded on the steel balls slid against the a-C:H DLC and the Si-doped DLC flats are presented in Figure 8.

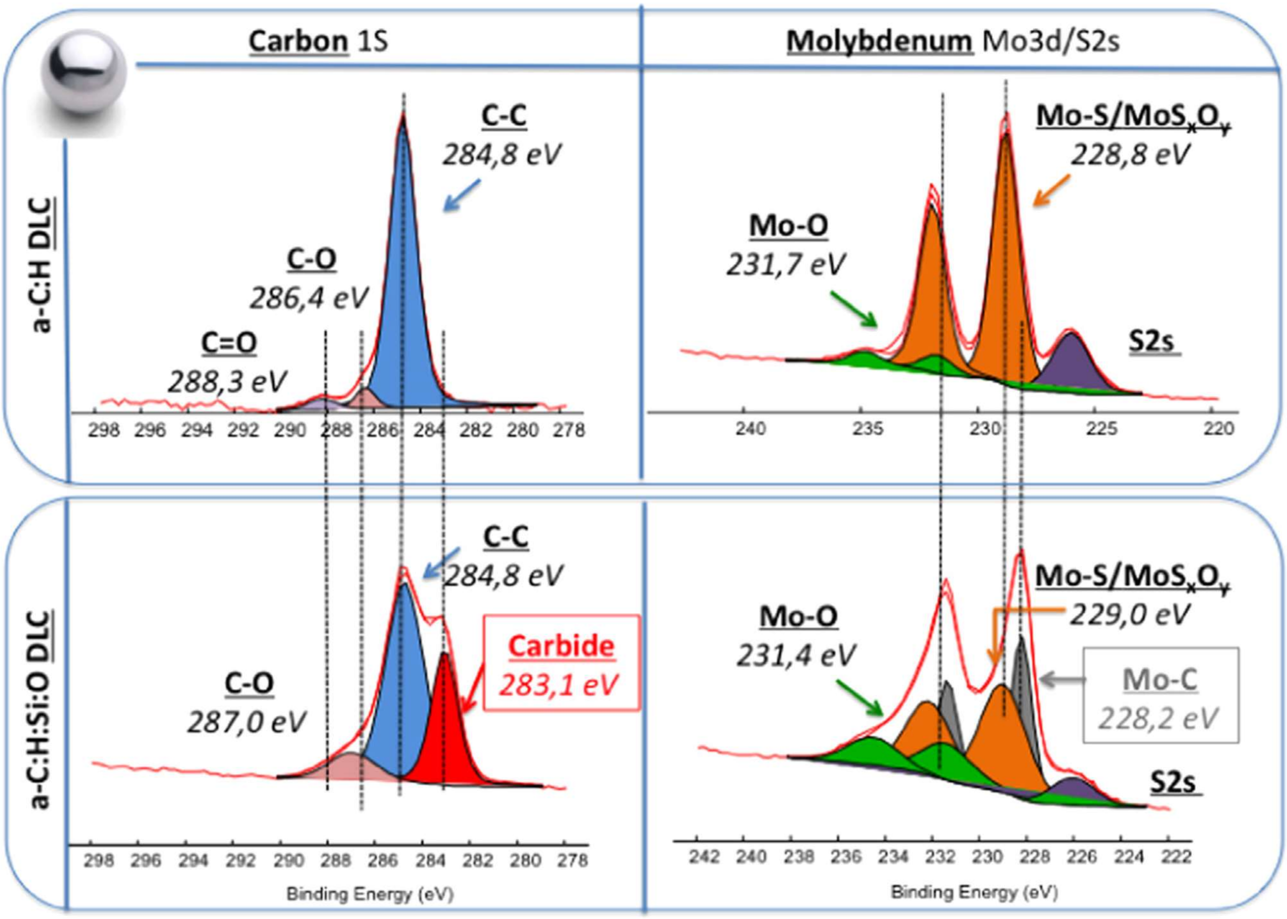


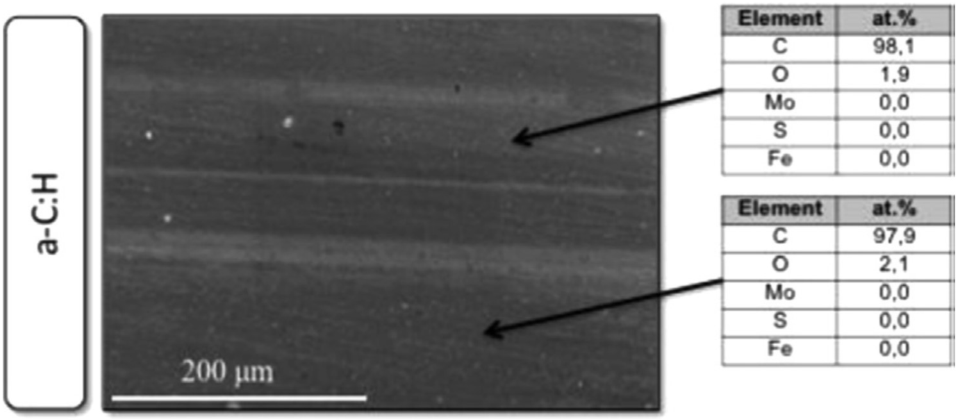
Fig 8. Curve fitting of C1s and Mo3d photoelectron peaks recorded on tribofilms formed on the steel counterparts rubbed against Hard a-C:H DLC and a-C:H:Si:O DLC using fresh MoDTC-containing oil.

The carbon peak related to the a-C:H DLC experiment clearly exhibits three contributions: the main peak at 284.8 eV, characteristic of the alkyl chain C-C, and two others located at 286.4 eV and at 288.3 eV, assigned to C-O bonds. In the case of the Si-doped DLC, the binding energies for C1s were found at 284.8 eV and 287.0 eV, also corresponding to C-C and C-O bonds, but a third contribution located at 283.1 eV was needed to fit the experimental spectrum properly. According to the literature, this peak position is attributed to carbide species [20]. The Mo3d XPS spectrum detected on the wear track of the steel ball sample rubbed against a-C:H DLC shows both Mo-S and Mo-O doublets observed at 228,8 eV and 231.7 eV, respectively, with FWHM of 1.4 eV (Figure 8). In the case of the tribofilm formed on the steel ball slid against the Si-doped DLC, the Mo3d fitting showed that besides formation of the same doublets located at 229.0 eV (Mo sulphide) and 231,4 eV (Mo oxide), molybdenum carbide is also clearly detected, as suggested by the presence of the peak at lower binding energy (228.2 eV).

The presence of molybdenum carbide species formed on the steel counter part after the experiment carried out on the Si-doped DLC is confirmed for both C1s and Mo3d XPS peaks.

3.4 Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX)

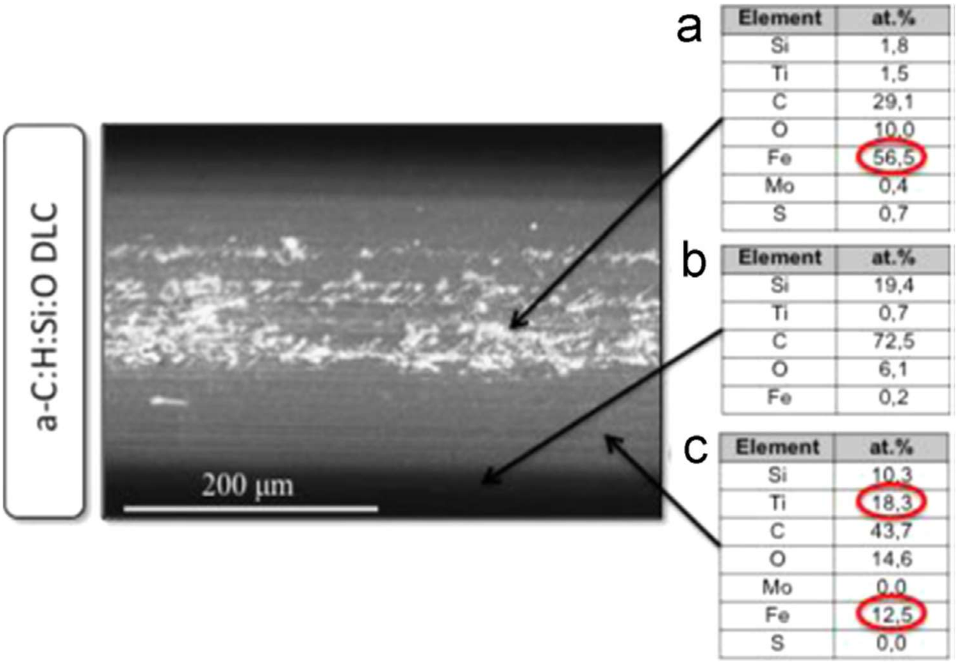
Figures 9 and 10 show SEM images and EDX analyses of rubbed and non-rubbed surfaces for a-C:H DLC coated flat and Si-doped DLC coupons, respectively.



Element	at.%
C	98,1
O	1,9
Mo	0,0
S	0,0
Fe	0,0

Element	at.%
C	97,9
O	2,1
Mo	0,0
S	0,0
Fe	0,0

Fig 9. SEM micrograph of the wear scar on a-C:H DLC -coated flat and the corresponding EDX atomic composition inside and outside the wear track.



a

Element	at.%
Si	1,8
Ti	1,5
C	29,1
O	10,0
Fe	56,5
Mo	0,4
S	0,7

b

Element	at.%
Si	19,4
Ti	0,7
C	72,5
O	6,1
Fe	0,2

c

Element	at.%
Si	10,3
Ti	18,3
C	43,7
O	14,6
Mo	0,0
Fe	12,5
S	0,0

Fig 10. SEM micrograph of the wear scar on Si-doped DLC-coated flat and the corresponding EDX atomic composition inside and outside the wear track.

According to the SEM image (Figure 9), the a-C:H DLC flat has a smooth appearance with only few slightly inhomogeneous zones on the wear scar. Carbon is the major element inside and outside wear scar. Regarding the Si-doped DLC (Figure 10), three different areas can be recognized revealing that high wear is produced:

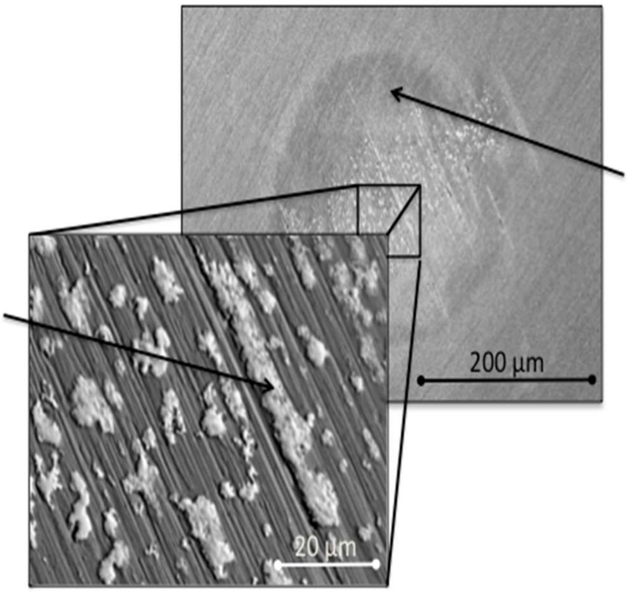
(1) white patchy areas that correspond to a high atomic number, revealing that the DLC is completely worn out and the steel substrate has started to emerge.

(2) a black area represents the original non-rubbed DLC, which is made of carbon and almost 20% of silicon; and

(3) grey areas in the wear scar which are due to the detectable titanium sub-layer, although there is still DLC coating present.

Figure 11 shows SEM images and chemical composition of worn surface on the steel ball after rubbing. Following EDX analysis results, the elemental composition in the dark grey region on ball wear scar is dominated by iron, demonstrating that the ball was worn out at this region (no tribofilm formed) suggests that there is the formation of tribofilm mainly containing carbon, molybdenum and iron.

Element	**at.%**
Mo	**21,3**
Si	1,6
Fe	17,4
C	**53,2**
O	5,3
S	1,0
Ti	0,2



Element	**at.%**
Fe	61,4
O	10,4
C	27,5
Si	0,4
S	0,3
Mo	0,0

Fig 11. SEM micrograph of the tribofilm formed on the steel ball rubbed against Si-doped DLC and EDX composition.

4. Discussions

4.1 Experimental results

To study the antagonistic interaction of MoDTC additive on DLC materials, different types of DLC coatings were tested in presence of base oil and fresh and aged oil containing MoDTC. Based on these experimental results it can be seen that adding 1wt% of MoDTC into the base oil leads to lower friction values in both steel/steel and DLC/steel contacts when the oil is fresh. The comparison of the degraded MoDTC-containing base oil on different DLC coatings (Figure 3) indicates that the ageing process can lead to a slight poorer MoDTC performance. In particular, employing aged oil the steady-state friction coefficient obtained was approximately 0.08, instead of 0.06-0.07 for the steel/steel contact for both fresh and aged oil. At the same time, it can be noted that the oil ageing process impacts less on DLC/steel contact than steel/steel contact. In fact, the DLC coating also gave lower friction coefficient than steel/steel during a test with 8 h degraded oil. This could be explained by considering that the reaction products produced during the degradation process [19] give a lower performance in steel/steel than DLC/steel contact. However, further analyses are needed to clarify the degradation impact on the tribological properties when DLC material is involved.

By comparing wear data for the DLC-coated flats lubricated with fresh and aged oils, it was found that the oil degradation tends to accelerate their wear rates. The comparison of the steady-state friction coefficients and wear rates obtained for the different steel/ DLC combinations (Figure 3 and 5) indicates that 4 DLCs displayed similarly good tribological performance, while the Si-doped DLC exhibits completely different behaviour, with high friction and wear.

SEM images carried out on a-C:H DLC/steel and Si-doped DLC/steel tribopairs, displaying completely opposite tribological behaviour, confirmed that a-C:H DLC is not damaged during the experiment. At the same time, the EDX analysis made on the Si-doped DLC reveals that catastrophic wear has been produced during the experiment, as suggested by the zone enriched in iron and titanium (DLC sub-layer). Furthermore, on the steel ball rubbed against Si-doped DLC were observed white patchy zones, rich in molybdenum and carbon.

The XPS analysis carried out after the friction experiments revealed that the $MoS_{2-x}O_x$ compounds, generally responsible for lower the friction coefficient, are mainly present on the tribofilm formed on the steel counterpart. Indeed, the amount of molybdenum detected on the surface of DLC coating was negligible. These results are coherent with the literature that has reported the absence of a Mo-containing tribofilm on the DLC surface [10]. Furthermore, no direct correlation was observed between the wear produced on the DLC coating and the Mo-oxides species detected by XPS. Considering this result, in the conditions employed in this work, Shinyoshi's model cannot be validated [5]. However, an interesting feature was observed on the C1s and Mo3d photopeaks, new contributions at about 283.1 eV and 228.2 eV, respectively (Figure 8), which only present on steel ball rubbed against Si-doped DLC. They can be attributed to Mo carbide species according to XPS database. This is consistent with the EDX analysis obtained on the Si-doped DLC/steel tribopair.

The comparison between our tribological experiments and XPS and SEM analyses provides valuable insights into the mechanisms underlying the severe wear of DLC material. The results suggest that when strong wear of DLC occurs, Mo carbides species could form on the steel counterpart. This carbide compound could result from the reaction between molybdenum present in the tribofilm formed on the steel ball counterpart during the few cycles of the friction experiment and the dangling surface carbon bonds of the DLC.

4.2 Proposal of new wear mechanism

According to the findings detailed in the previous sections, a new mechanism for the wear of DLC in presence of MoDTC-containing oil can be proposed. This new wear model is schematized in Figure 12.

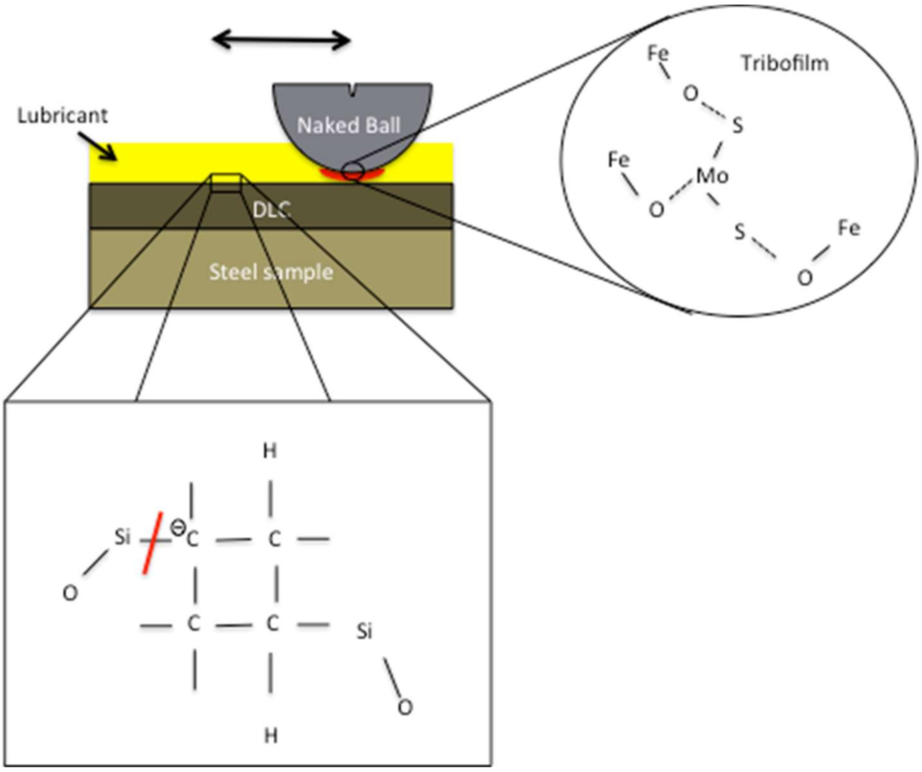


Fig 12. Schematically representation of the new wear model proposed.

The first phase of the scenario involves two, probably simultaneous, steps. Considering that Mo-S XPS contribution was only found in wear scar regions on the steel balls and not on the DLC-coated flats, there is strong evidence for the key role of the steel surface for the MoDTC decomposition to form MoS_2 layers and/or $MoS_{2-x}O_x$ compounds, depending on the degradation level of the oil [13].

For this reason, it can be supposed that the formation of a molybdenum-based tribofilm on the steel surface is the first step in the DLC wear mechanism. At the same time, during the friction experiment, the temperature and the mechanical stresses can lead to the breaking of Si-C bonds network present in the Si-doped DLC structure. Subsequently, the molybdenum contained in the tribofilm formed on the steel ball may react with the carbon dangling bonds created on the DLC surface, resulting in the molybdenum carbides (Mo_xC) formation on the naked steel ball. In other words, it is supposed that there is a chemical grabbing of carbon from the DLC coating through the steel counterpart thanks to the reaction with molybdenum species present on the steel ball tribofilm.

4.3 Model validation

To confirm the wear scenario proposed above, additional friction experiments and surface analyses were carried out. The hypothesis about the formation of MoS_2 and/or $MoS_{2-X}O_x$ compounds on steel counterpart during the first cycles of the experiment and the consequent reaction between the molybdenum and carbon from the DLC leading to the formation of molybdenum carbide species inside the contact is supported by considering the “variable duration tests” for Si-doped DLC/steel tribopair. Figure 13 shows the evolution of the friction coefficient as function of test duration for the different oils tested. As can be noted, in the beginning of the test carried out with fresh oil, there is an immediate and significant reduction in friction, followed by a sharp increase, reaching a value similar to the additive-free base oil, 0.12. The “variable duration tests” consist of stopping the test in the “low friction regime (a)” and when the friction coefficient starts to be high “(b)”. The XPS spectra recorded on the steel balls wear tracks after these short tests against the Si-doped DLC coating (Figure 14) clearly show that during the first cycles, when the friction coefficient is relatively low due to the formation of MoS_2 compounds, no carbide formation is detected on the steel ball counterpart (Figure 14a). The peak corresponding to the carbide starts to appear only when the high friction regime is reached (Figure 14b) and it increases with the sliding duration (Figure 14c).

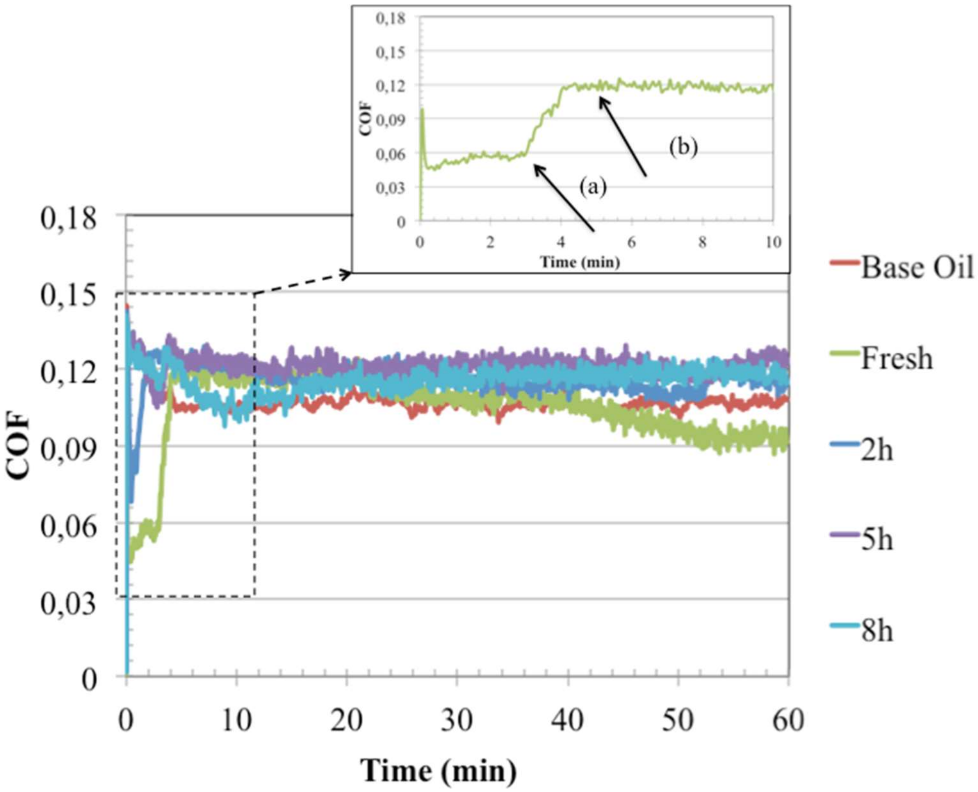


Fig 13. Friction behaviour for the Si doped DLC for fresh and aged MoDTC-containing oils. In the zoom it is visible the low friction regime (a) and the high friction regime (b).

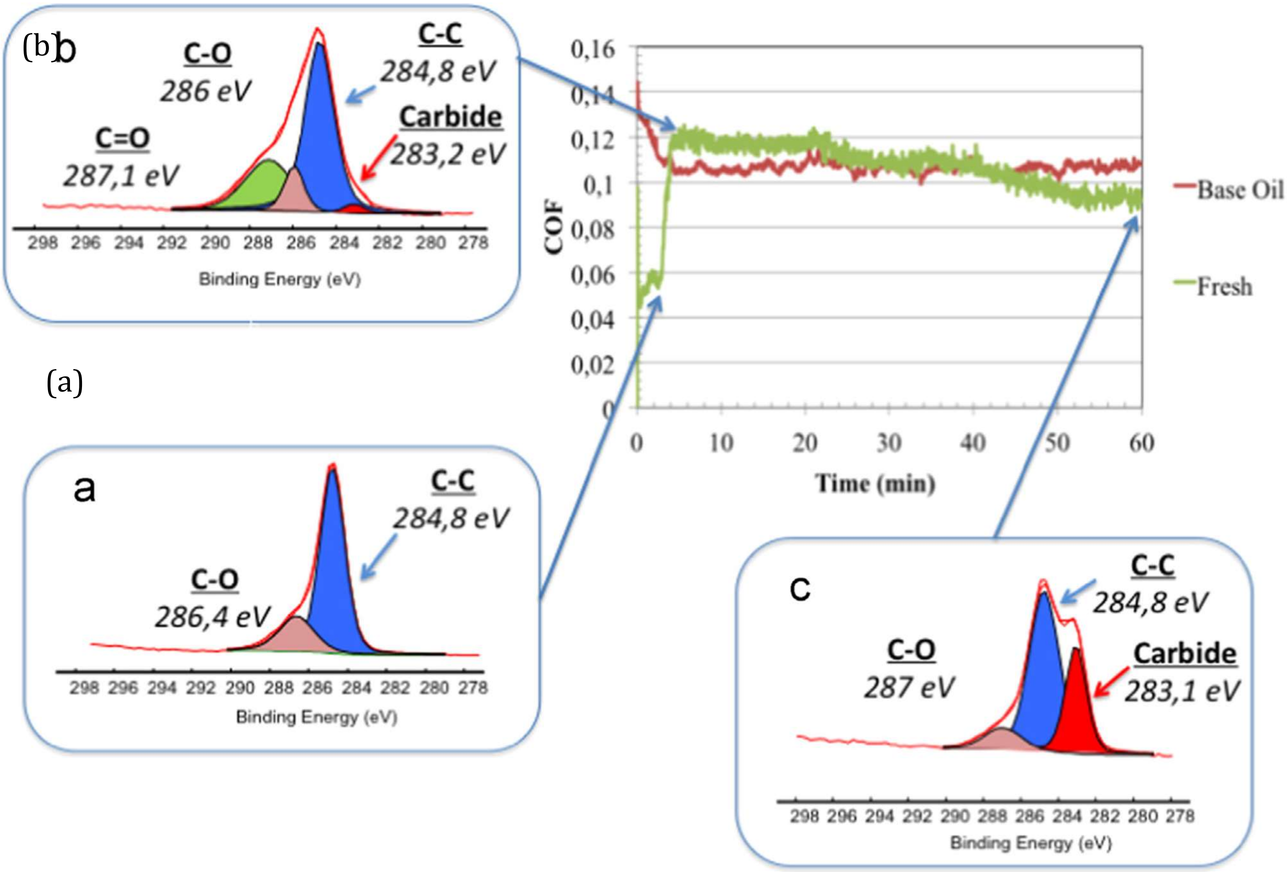


Fig 14. Curve fitting of C1s photopeaks recorded on tribofilm formed on the steel ball counterpart rubbed against Si doped DLC in the presence of fresh MoDTC-containing oil. The test is stopped during the low (a) and high (b,c) friction regimes.

The relation between the carbide occurrence inside the contact and the high-friction regime is further confirmed by the SEM images of worn surface of the steel balls after sliding against Si-doped DLC (Figure 15). Indeed, the presence of white patchy zones, rich in molybdenum and carbon, is only evidenced when high friction regime is reached (figure 15(b)).

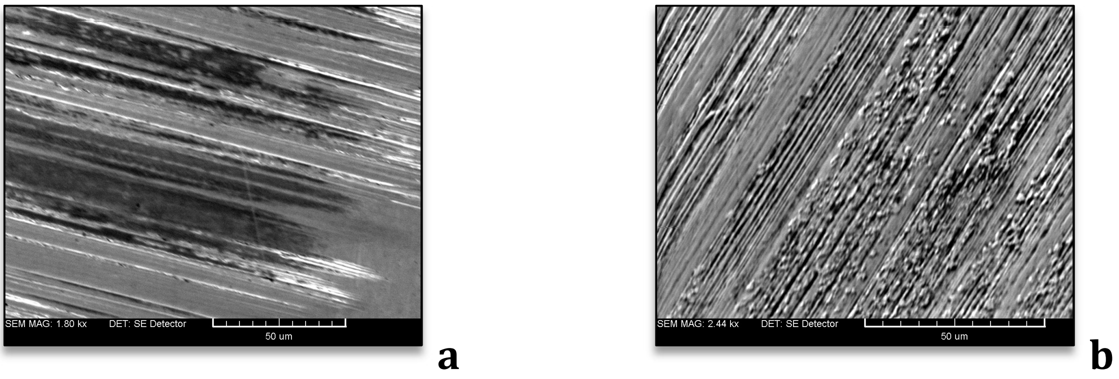


Fig 15. SEM images of the wear scar on the steel ball counterpart rubbed against Si doped DLC after variable test duration: low friction regime (a) and high friction regime (b).

The other question arising from the wear mechanism hypothesized is why the Si-doped DLC shows high wear while the a-C:H DLC, under the same test conditions, does not show similar behaviour. To answer this question, the Bond Dissociation Energy (E) (or Potential Energy) of the different chemical species is considered. It is possible that, in the conditions employed in the friction experiment (temperature, pressure and time) and considering the complexity of the DLC structures, the energy dissipated inside the contact is enough to break C-Si bonds but not or the other chemical bonds. The decomposition of silicon and carbon atoms at the worn Si doped-DLC surface due to the tribo-process has already been reported [16]. The authors investigated the performances of the pure DLC and Si-doped DLC coatings in dry conditions and found that the interaction between Si-doped DLC and the steel counter body induces higher wear rate in comparison with non-doped DLC coating. To verify this point, experiments with higher applied loads were carried out to dissipate more energy at the interface of the a-C:H DLC/steel tribo-pair. The wear rates measured for a-C:H DLC as a function of the load are reported in Figure 16.

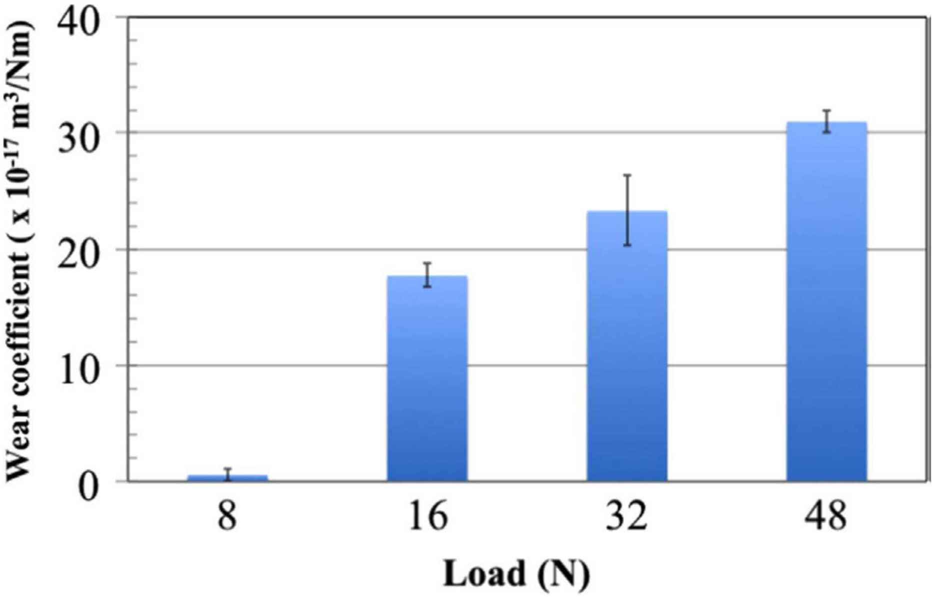


Fig 16. Wear coefficient vs. load for the A.Carbon DLC coating.

There is a clear correlation between the load and wear rate: the higher the load applied, the higher the wear rate is. The comparison of C1s and Mo3d photopeaks recorded on the steel ball counterparts after the tests carried out at 8 N and 48 N confirm the presence of carbide compounds only for higher loaded tests causing higher wear (Figure 17). This result could be explained with a more important interaction between the DLC and the reaction products of the MoDTC degradation. A detailed investigation is required to confirm this hypothesis and it will be the topic of a future publication.

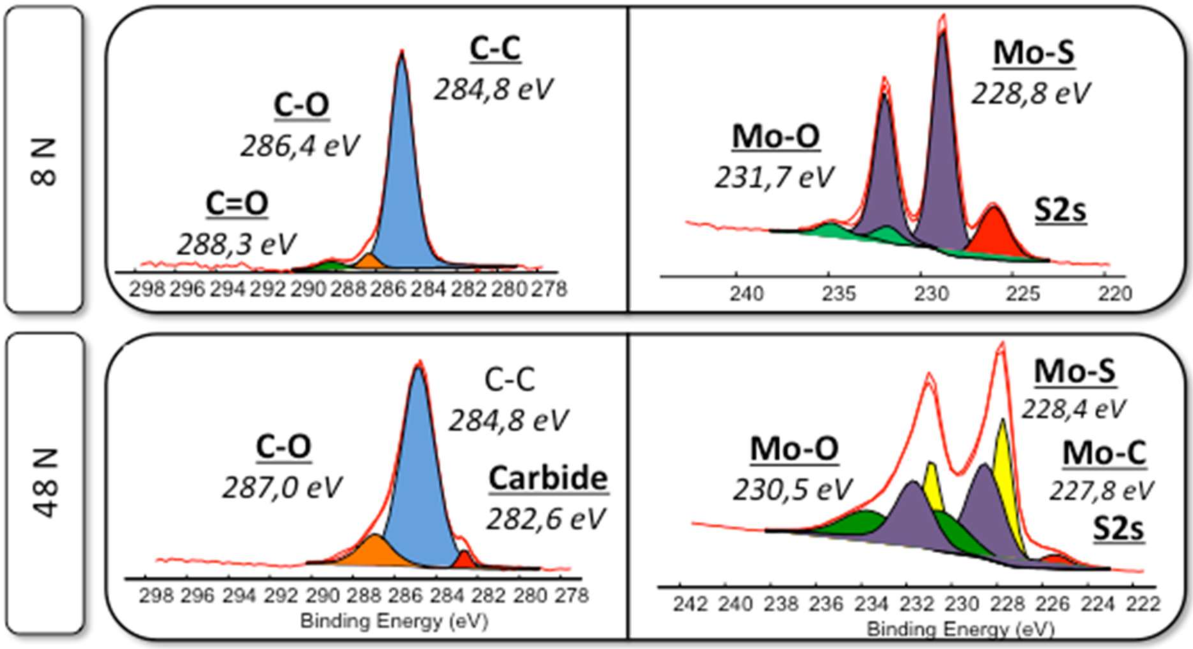


Fig 17. Curve fitting of C1s and Mo3d contributions obtained from tribofilm formed on the steel counterpart rubbed against Hard a-C:H DLC coated flat using fresh MoDTC-containing oil. The test is carried out using 8 N and 48 N pressure.

5. Conclusions

In this study, the boundary lubrication of different DLC coatings is investigated in mild wear conditions in the presence of MoDTC additive. A number of these coatings show the effective performance of the MoDTC additive in reducing friction coefficient compared to additive-free base oil. However, the silicon and oxygen doped DLC coating (Si-doped DLC) is the only one showing relatively high friction combined with dramatic wear.

The degradation of MoDTC-containing base oil has less impacts on the DLCs/steel contact than the steel/steel one. Indeed, after 8 hours of oil ageing it is still possible to have friction reduction with some DLC coatings even if higher wear is produced in comparison with the fresh oil.

The severe wear of DLC coatings lubricated with MoDTC has been widely reported in the literature by different authors, but the major cause of it was not clearly identified yet. All the tribological experiments and analytical results of this work provide strong support to the conjecture that the formation of a molybdenum carbide compound is an important step in mechanism governing the wear of DLC coatings sliding against a steel counterpart in the presence of MoDTC additive. The formation of this carbide compound is evidenced for the first time on the steel counterpart surface. A new wear scenario is prosed, consisting of different steps:

1. During the initial running-in period, MoDTC additive reacts preferentially with steel surface, forming a MoS_2 and/or $MoS_{2-x}O_x$ based tribofilm on the steel, compounds able to lower the friction coefficient.
2. During further sliding, this molybdenum-based tribofilm interacts with the carbon dangling surface bonds of Si-doped DLC generated by breaking of the Si-C bond network;
3. The reaction between molybdenum present in the tribofilm formed on the steel counterpart and the carbon of the DLC coating leads to the formation of molybdenum carbide (Mo_xC) species resulting in an increase in friction and wear rate, as suggested by the surface analyses.

Further studies will be performed to obtain more structural information about the molybdenum carbide species formed on the steel counterpart by tribochemical reaction in the presence of MoDTC friction modifier additive. Moreover, it is important to check if the DLC wear process in the presence of the MoDTC also involves the well-established re-hybridization change of the DLC coating leading to the formation of softer amorphous sp^2-carbon rich a-C material layer, which may contribute to the rapid wear.

6. Bibliography

[1] Yamamoto Y., and Gondo S., (1989), “Friction and Wear Characteristics of MoDTC and MoDTP”, Trib. Trans., 32, pp.251-257.

[2] Moore F.W., and Larson M. L., (1967), “Dialkyldithiocarbamate Complexes of Molybdenum (V) and Molybdenum (VI)”, Inorg. Chem., 6, pp.998-106.

[3] Robertson J. Diamond-like amorphous carbon. Materials Science & Engineering R- Reports. 2002 May;37(4-6):129-281.

[4] Andersson J, Erck RA, Erdemir A. Friction of diamond-like carbon films in different atmospheres. Wear. 2003;254(11):1070-5.

[5] Shinyoshi T, Fuwa Y., Ozaki Y., “Wear analysis of DLC coating in oil containing Mo-DTC”, JSAE 20077103, SAE 2007-01-1969.

[6] Haque T; Morina A; Neville A; Kapadia R; Arrowsmith S Effect of oil additives on the durability of hydrogenated DLC coating under boundary lubrication conditions. Wear, vol. 266, pp.147-157, (2009).

[7] Kubo K, Mitsuhiro N., Shitamichi T., Motoyama K, “The effect of ageing during engine running on the friction reduction performance of oil soluble molybdenum compounds”, Proceeding of the international tribology conference, Yokohama, (1995).

[8] De Barros Bouchet M.I., Martin J.M., Le Mogne Th., Bilas P., Vacher B., Yamada Y., Mechanisms of MoS2 formation by MoDTC in presence of ZnDTP. Effect of oxidative degradation. Wear, 258, Pp. 1643, (2005).

[9] Masabumi M., Takuya O., Saiko A., Akihito S., Hirotaka I., Friction and wear characteristics of DLC coatings with different hydrogen content lubricated with several Mo-containing compounds and their related compounds, Tribology International, vol. 82, part B, pages 350–357, (2015).

[10] Kosarieh S; Morina A; Lainé E; Flemming J; Neville A The effect of MoDTC-type friction modifier on the wear performance of a hydrogenated DLC coating. Wear, vol. 302, pp.890-898, (2013).

[11] I. Sugimoto, F. Honda, K. Inoue, “Analysis of wear behavior and graphitization of hydrogenated DLC under boundary lubricant with MoDTC”, Wear, Volume 305, Issues 1–2, 30 July 2013, Pages 124-128

[12] M.I. De Barros Bouchet, C. Matta, B. Vacher, Th. Le-Mogne, J.M. Martin, J. von Lautz, T. Ma, L. Pastewka, J. Otschik, P. Gumbsch, M. Moseler, Energy filtering transmission electron microscopy and atomistic simulations of tribo-induced hybridization change of nanocrystalline diamond coating, Carbon 06/2015; 87.

[13] M. De Feo, C. Minfray, M.I. De Barros Bouchet, B. Thiebaut, Th. Le Mogne, B. Vacher, J.M. Martin, “Ageing impact on tribological properties of MoDTC-containing base oil”, Tribology International 92, 126–135, (2015).

[14] Moulder JF, Stickle WF, Sobol PE, Bomben KD. Handbook of X-ray Photoelectron Spectroscopy: Physical Electronics, Inc. 1995.

[15] Katsuhiko Oshikawa , Masatoshi Nagai ,* and Shinzo Omi, Characterization of Molybdenum Carbides for Methane Reforming by TPR, XRD, and XPS, J. Phys. Chem. B, 2001, 105 (38), pp 9124–9131.

[16] K. Oguri and T. Arai, Tribological properties and characterization of diamond-like carbon coatings with silicon prepared by plasma-assisted chemical vapour deposition, Surface and coating Technology, 47 (1991), 710-721.

[17] R.T.Vanderbilt, Molybdenum-containing dithiophosphoric ester compounds, UK Patent 1144145, 1966.

[18] T.Sakurai, H.Okabe, H.Isoyama, The synthesis of di-m-thio-dithio-bis (dia - lkyldithiocarbamates) dimolybdenum(V) and their effects on boundary lubrication, Bull. Jpn. Pet. Inst. 13(1971), 308–314..

[19] M. DeFeo, C. Minfray, M.I.De Barros Bouchet, B. Thiebaut, J.M. Martin, MoDTC friction modifier additive degradation. Correlation between chemical changes and tribological

performances, RSCAdv.5(2015) 93786–93796.

[20] D. Briggs, M.P.Seah (Eds.), seconded., Practical Surface Analysis, vol.1, John Wiley &Sons, NewYork, NY, USA, 1993.

[21] K. Oguri and T. Arai, Tribological properties and characterization of diamond-like carbon coatings with silicon prepared by plasma-assisted chemical vapour deposition, Surface and coating Technology, 47 (1991), 710-721.

[22] C.D. Wagner, L.E.Davis, M.V.Zeller, J.A.Taylor, R.H.Raymond, L.H.Gale, Empirical atomic sensitivity factors forquantitative analysis by electron spectroscopy for chemicalanalysis, Surf. Interface Anal. 3(5) (1981), 211–225.

7. Acknowledgements

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