Formation of interfacial molybdenum carbide for DLC lubricated by MoDTC: Origin of wear mechanism.

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ABSTRACT: A large amount of research has been devoted to the effect of molybdenum dithiocarbamate (MoDTC) additives on the lubricating performances of carbon-based coatings, showing that high wear rate is produced when the MoDTC is blended to the base oil. However, the mechanisms leading to the coating removal are not fully understood yet.

In this work, the friction and wear performances of amorphous hydrogenated DLC coating doped with silicon and oxygen have been analysed when lubricated by MoDTC-containing oils. The tribological experiments have been conducted with DLC/steel and DLC/DLC contacts under boundary lubrication conditions using a ball-on-flat tribometer. To understand the wear mechanism, the chemical composition of the tribofilm formed on the steel ball counterpart was investigated by X-ray Photoelectron Spectroscopy (XPS). Transmission Electron Microscopy (TEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDX). A new DLC wear model has been proposed and validated.

1. Introduction

Many recent works have shown that Diamond-like carbon (DLC) coatings provide an optimal combination of relatively high hardness, chemical inertness and low friction and wear [1].

In recent years, a large number of studies have been devoted to the improvement of DLC coating performance. Particularly, to enhance the properties of DLC films, different chemical elements or compounds (nitrogen, silicon, titanium, tungsten etc.) have been added into the coating [2,3]. Among them, amorphous hydrogenated silicon- and oxygen-doped DLC films (a-C:H:Si:O) have attracted special attention due to their ability to decrease residual internal stress without sacrificing

the hardness of the coating [4,5]. This is because the coating has improved resistance to oxidation and adhesion to metal alloys, steels and glasses, leading to better high temperature stability [6-8]. Due to these interesting properties, this type of DLC has been studied in the last few years for application in different fields. Great effort has been expended in the development of a carbon-based coating containing silicon and oxygen to be employed on automotive parts. Therefore, it is extremely important to optimize the interaction between a-C:H:Si:O DLC and the additives present in the modern engine lubricants to further reduce its already low friction coefficient. Molybdenum Dithiocarbamate (MoDTC) is a well-known friction modifier additive that decomposes during the tribo-test under heating, generating molybdenum disulphides (MoS_2) and molybdenum oxide (MoO_3) species [9]. Although the exact mechanisms are not fully understood yet, it is well accepted that the low friction coefficient is brought about the interaction between MoS_2 lamellar sheets in the generated tribofilm [10].

The changes in the coating structure under lubrication with MoDTC-containing oil have been extensively investigated in recent years [11-13]. The antagonism between the DLC coating and the MoDTC friction modifier, causing catastrophic high wear rate, has already been reported several times. On the other hand, although some wear models have been proposed [11,12], there is still a lack of understanding of the fundamental wear mechanisms. In fact, there are strong disagreements in the literature covering this aspect: the DLC wear has been explained both by abrasive wear caused by MoO_3 hard particles [11] and by a graphitization process occurring on the top surface of the DLC [14,15]. Shinyoshi et al. [11] and Haque T. et al. [12] tried to justify the high wear obtained on the DLC samples when lubricated by MoDTC by the interaction between the coating and the molybdenum oxide derived from the additive decomposition during the tribotest. However, the relation between MoO_3 and the wear rate of DLC coating has already been rejected by different authors [16]. It has also been demonstrated experimentally [14,15] and using dynamic simulation [15] that the severe tribotest conditions (temperature, pressure and mechanical stress) can induce re-hybridization changes from sp^3 to sp^2 in the electronic structure of carbon. This transformation can

lead to a faster removal of the DLC top surface, causing the coating failure. So far, however, the evidence for a direct relation between MoDTC and the chemical changes in the C-C bond has not been clearly explained yet.

In a previous study [17], preliminary results were reported for the first time, and a new wear model based on the formation of molybdenum carbide species has been proposed. In particular, tribological experiments combined with X-ray photoelectron spectroscopy (XPS) surface analyses have revealed the presence of Mo-C bonding on the steel counterpart. For this reason, it has been proposed that the main wear mechanism responsible for the DLC failure when lubricated by MoDTC-containing oil is a chemical origin. It is suggested that there is a chemical reaction between the molybdenum present in the tribofilm formed on the steel ball and the dangling carbon bonds of the DLC derived from the breaking of carbon-silicon bond.

A brief summary of the most relevant results described the proposed model are shown in the results paragraph.

This study provides strong support for the conjecture that the formation of a Mo-containing tribofilm material on the steel counterpart is at the origin of the mechanism governing the wear of DLC coatings. It remains, however, unclear whether such MoC_x species can cause such dramatic wear, and particularly if this is related to their structure and mechanical properties.

Although XPS analyses are able to detect the presence of MoC_x species on the rubbed surfaces, it is possible to infer the underlying mechanism from analytical results alone. In recent work, after a brief summary of the most relevant results described in [17], we address the validation of the new proposed wear model using microscopic and mechanical tools.

A Transmission Electron Microscopy (TEM) study coupled with Energy Dispersive X-Ray Spectroscopy (EDX) and Selected Area Electron Diffraction (SAED) analysis has been employed to analyse the structure of the tribofilm formed on the steel ball to confirm the presence of molybdenum carbide. Furthermore, to evaluate if the MoC_x-containing tribofilm formed on the steel ball is much stiffer than the DLC coating, nano-indentation tests were performed on the tribofilm to

demonstrate whether the DLC wear is caused by an abrasive mechanism. Finally, the key role of the steel counterpart in the proposed mechanism has been validated by considering the DLC/DLC contact configuration.

2. Materials and methods

2.1. Material

2.1.1. Lubricant

A standard mineral oil belonging to group III was used as base lubricant. The viscosity of this base oil is 20 cSt at 40°C. The chemical structure of the molybdenum dithiocarbamate (MoDTC) used as friction modifier additive is shown in Figure 1. In the schematic formula X can be S or O atoms (although mainly S) while and R is a mixture of C_8 and C_{13} alkyl chains. The concentration of MoDTC friction modifier used is 1wt%. The additive is blended to the base oil by heating and stirring the solution at 65°C for 10 minutes. Tests were made at least three times using the oils, both with and without MoDTC.
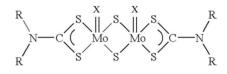

Fig. 1. Chemical structure of molybdenum dithiocarbamate (MoDTC).

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2.1.2. a-C:H:Si:O DLC coating

Amorphous hydrogenated diamond-like carbon coating doped with silicon and oxygen (a-C:H:Si:O) was deposited on the polished AISI 52100 steel by plasma enhanced chemical vapour

deposition (PECVD). An adhesion-promoting titanium sub-layer was first deposited on the steel plate. The material properties of the DLC coating and the steel are given in Table 1.

Properties of coating/material	Uncoated steel substrate and steel counterbody	a-C:H:Si:O coated steel plate
Specification	AISI 52100	PACVD Si & O doped DLC with Ti adhesion layer
Thickness of the coating	-	ca. 2.0 μm
Thickness of Ti adhesion layer	-	ca. 0.3 μm
Hardness (GPa)	10	18-20
H% content (approximately)	-	25-35
Roughness	Ra<0.05 μm	Ra<0.05 μm

Table. 1. Principal properties for the steel and the DLC materials.

2.2. Methods

2.2.1. Tribotest

The tribological experiments were conducted using reciprocating linear ball-on-flat tribometer on both DLC/Steel contact, i.e. with AISI 52100 steel ball (6.7 mm radius) against a DLC-coated flat coupon, and DLC/DLC tribopairs.

The boundary condition is reached using a combination of parameters. A load of 8 N is applied resulting in a maximum contact pressure about 770 MPa. The average speed is 5 mm/s, with a stroke length of 5 mm. The duration of the test is 1 h at 100°C. At this temperature, the calculated minimum EHL film thickness is less than 1 nm, much smaller than the composite roughness of the two surfaces. Therefore the lambda ratio is well below unity and the lubrication regime is boundary.

To remove any dust from the initial surfaces, both coated flat and steel ball samples were cleaned before each test using *n-heptane* solvent in an ultrasonic bath for 10 min.

The friction experiment has been repeated three times and the reproducibility is fairly good.

2.2.2. X-ray Photo Spectroscopy (XPS)

The elemental composition of the top surface (typically depth of 10 nm) and the nature of the chemical bonds between the elements have been investigated by XPS. The apparatus is an PHI-ULVAC VersaProbe II, integrated with a monochromatized AlKα X-ray source (1486.6 eV). The X-ray beam focused on the wear scar of an area of 50 μm x 50 μm, probing a depth of only a few nm. The energy scale was calibrated with reference to the C1s line at BE = 284.8 eV. First, XPS measurements were taken over a survey spectrum covering a range of 1200 eV, to identify all peaks and the presence of contaminants. Afterwards, a scanning of the individual peaks in more detail over a smaller range of 15-25 eV was undertaken. The detailed spectra of the elements identified are acquired to establish the different chemical states of the species and to perform a quantitative analysis using PHI multipack software. The chemical species corresponding to each binding energy were determined using standard materials, the XPS handbook [18] and online database [19]. The XPS photo-peaks were fitted with a Shirley background, and the quantification is calculated with Wagner sensibility factors [20].

Depth profiling for the tribofilm on the steel ball rubbed against the a-C:H:Si:O DLC was also conducted using 1 kV Ar^+ bombardment. .

2.2.3. Nano-indentation

The mechanical properties of the DLC coating, the tribofilm generated on the steel ball counter-part, and the steel substrate are measured by means of nano-indenter from MTS. The nano-indentation experiments were conducted in different zones directly on the tribofilm formed on the steel ball. This system is equipped with an optical microscope, through which it is possible to choose a desired area for the measurement.

The indentations were carried out using a Berkovich-type tip geometry in a dynamic mode (loading rate of 0.03 s^{-1}). Hardness vs. penetration-depth curves were recoded using a maximum load of 450 mN. The experiments were performed at least at three times on the different locations chosen.

2.2.4. Transmission Electron Microscope (TEM)

The detailed microstructural characterization of the tribofilm formed at the worn steel ball rubbed against DLC coating was performed using the Focus Ion Beam (FIB) cross-section. Prior to sectioning the cross-section, the tribofilm was protected with platinum layers. The analysis of the wear particles collected on a carbon grid has also been considered. Microscopic observations were taken in a 200 kV acceleration voltage Transmission Electron Microscope (JEOL 2010 F HR-TEM) equipped with Energy Dispersive X-Ray Spectroscopy (EDX). Thus, the four classical techniques have been employed: Selected Area Electron Diffraction (SAED) for the crystallographic determination of the crystallized compounds; Electron Imaging up to high magnification, the so-called High Resolution Imaging; Elemental chemical mapping using EDX spectroscopy and high Annular Dark Field imaging (HAADF) for chemical compound revelation.

3. Results

3.1. Characterisation of pristine a-C:H:Si:O DLC cooating

A preliminary study was conducted to investigate the structure of the DLC film, interms of the elemental chemical composition and bond hybridization. These results on the pristine DLC material, along with the other characterizations made in this study, enable the improvement of the new proposed wear model.

3.1.1. XPS analysis of pristine DLC coating

The Si2p photo-peaks recorded on the DLC-coated flat coupon prior to the tribo-test are shown in Figure 2. The fitting has been done using four contributions at 100.8 eV, 102.1 eV, 103.6 eV and 105.5 eV, corresponding to the different oxidation states of silicon.
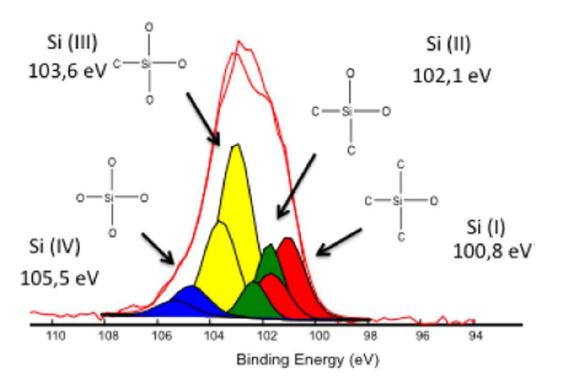

Fig. 2. XPS spectrum for Si2p for the a-C:H:Si:O DLC coating prior to the tribological characterization.

3.1.2. TEM observations

The low-magnification image of the silicon- and oxygen-doped DLC coating displayed in Figure 3 shows the multi-layer structure of this coating. The first layer, starting from the top-left, is the steel substrate, followed by a titanium interlayer used to improve adhesion. Finally, below the black platinum layers deposited to protect the surface during the FIB specimen preparation, a 1.4 μm thick DLC layer can be identified. To obtain more information about the DLC structure, EDX component maps were generated for carbon (C), oxygen (O), silicon (Si), titanium (Ti) and platinum (Pt) (Figure 4). Due to the presence of contaminants, meaningful maps could not be

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obtained for the carbon. However, it is possible to obtain an elemental distribution within the region of interest. The homogeneous distribution of silicon inside the DLC coating can be noted.
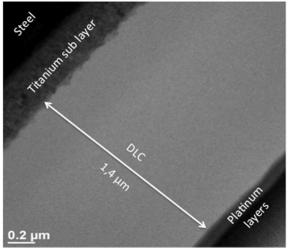

Fig. 3. Low magnification TEM image of DLC coating cross section.
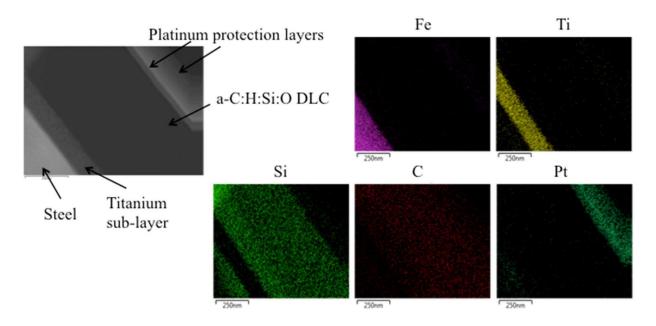

Fig. 4. EDX mapping revealing the multi-layered structure of DLC cross-section.

3.2. Evidence of DLC wear induced by MoDTC additive

3.2.1. Tribological behaviour

The friction coefficient as a function of time and the wear rate measurements obtained in he presence of the mineral base oil, with and without MoDTC additive, are shown in Figure 5.
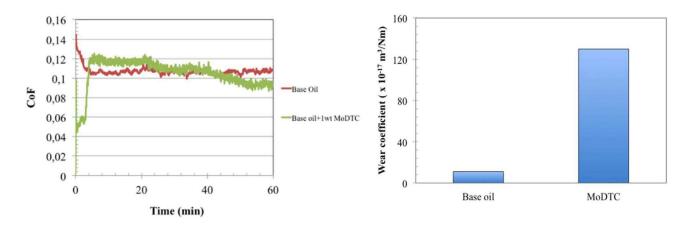
Fig. 5. Friction coefficient and wear rate measured on the DLC coating for the friction pair a-C:H:Si:O DLC/steel lubricated by base oil, with and without MoDTC.

It can be observed that MoDTC-containing oil provides an important friction reduction only during the first cycles. This result is repeatable even if the length of the low-friction period can vary. Afterwards, a steady-state friction coefficient similar to that obtained with the additive-free base oil is demonstrated. It is believed that, during the first part of the test, a molybdenum oxisulfide (MoSxOy)-based tribofilm formation takes place. This happens mainly on the steel counterpart, and it is responsible for the short friction reduction. Furthermore, when a MoDTC-containing base oil is employed, much higher wear on the DLC-coated flat coupon is obtained. In a previous paper [17], it was shown that the a-C:H:Si:O DLC presents the worst tribological behaviour compared to other hydrogenated DLC coatings tested under the same conditions, confirming the clear antagonism between MoDTC and Si-doped-DLC in steel/DLC contacts already reported in previous study [21].

3.2.2. XPS analysis of the rubbed surfaces

X-ray Photoelectron Spectroscopy (XPS) analysis was employed to study the chemical composition of the tribofilm formed on the wear scars of both the coated flat coupon and steel ball. All XPS analyses were performed at the end of the tribological tests. It has been observed that molybdenum-related peaks were not detected on the DLC sample (Figure 6).

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On the other hand, the analyses performed on the wear scar of the steel ball are shown in Figure 7. They revealed the presence of carbon, oxygen, molybdenum, iron, sulphur and traces of silicon. On Mo3d and C1s peaks, contributions can be attributed to carbide species, with C-Mo bonding in both carbon (C1s) and molybdenum (Mo3d) photo-peaks together with the more common C-C, C-O, Mo-S and M-O contributions.
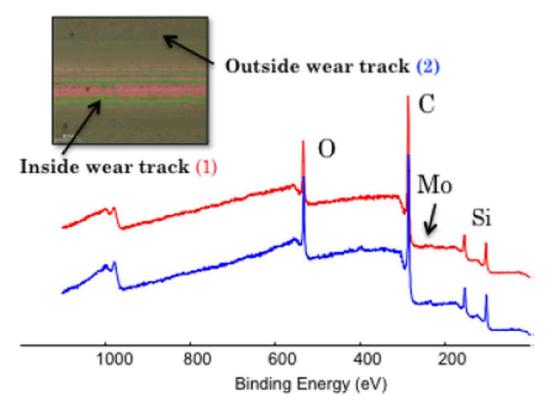

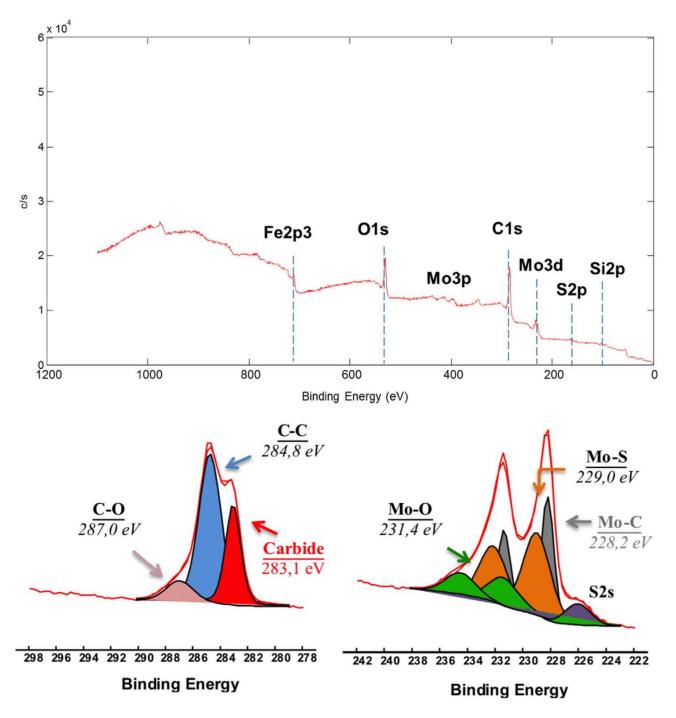**Fig. 6. XPS survey spectra for the a-C:H:Si:O DLC coated flat coupon.**

Fig. 7. XPS survey and C1s and Mo3d spectra for the tribofilm formed on the steel counterpart rubbed against an a-C:H:Si:O DLC coating.

3.3. Characterization of the tribofilm generated on the steel counterpart

Further accurate investigations of the tribofilm generated on the steel ball counterpart are needed to obtain deeper insights into the wear process of the DLC coating. Therefore, a methodology combining an XPS sputtering profile and TEM technique coupled with EDX and SAED analyses

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was used to perform a detailed characterization of the tribofilm formed on the steel ball counterpart slid against a-C:H:Si:O DLC.

3.3.1. XPS sputtering profile

To obtain more information about the Mo and C element distribution inside the tribofilm, XPS depth profiles were taken on the tribofilm formed on the steel ball slid against the a-C:H:Si:O DLC (Figure 8 and Figure 9). It can be seen that after 40 sputter cycles (28 min), the majority of the carbon contamination has been removed, while the peak corresponding to the carbide species becomes predominant. Taking into account that the presence of the molybdenum carbide species is still clear in the Mo3d contribution after the sputtering time, it is possible to confirm the main presence of MoC_X species in the whole tribofilm formed on the steel ball. Please note that the spectra are slightly shifted to lower binding energy in Figure 9, certainly due to an increase of the carbides contribution. However some artefacts due to the ion sputtering cannot be excluded.
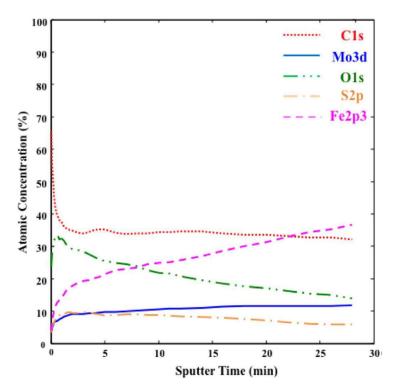

Fig. 8. XPS depth profiles of the tribofilm formed on the steel ball rubbed against an a-C:H:Si:O DLC coating.
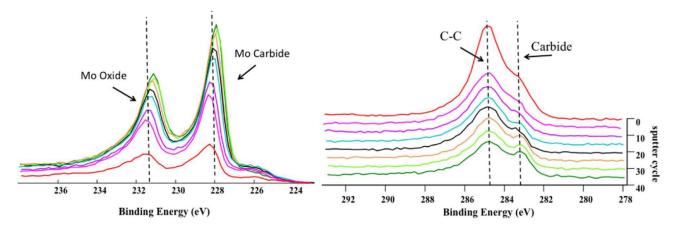
Fig. 9. XPS spectra zoomed in the molybdenum and carbon energy region (each color is associated with a sputter cycle number and vertical lines correspond to standard peak contributions).

3.3.2. TEM analysis

The ability to directly image a cross-section of the tribofilm formed on a steel ball by means of FIB coupled with TEM and the possibility to monitor its chemistry using EDX analysis have been employed to obtain more information about the interaction between the DLC coating and MoDTC additive. The TEM specimen has been prepared by selecting a specific region of the steel ball surface to include the white patchy areas (see the red rectangle in Figure 10).
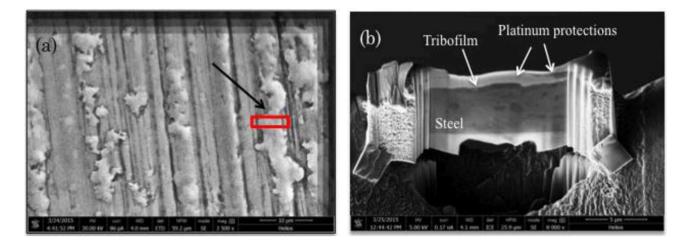

Fig. 10. SEM images of the tribofilm formed on the steel ball after a tribotest against the a-C:H:Si:O DLC (a) and cross-section of the layered structure of the cross-section performed in the zone (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.

Figure 11 shows a High Angle Annular Dark Field (HAADF) image of the tribofilm. A strong Z-contrast of elements is shown in the tribofilm (the lowest is the atomic number, the darker is the contrast), and the transverse bands are due to thickness variations of the FIB thin foil. The zoomed image in Figure 11 shows that different layers can be distinguished: the region on the top represents the platinum protection layer used to avoid damage during the sample FIB production, the 0.5 μm thick area represents the tribofilm, and the last layer is the steel.

HAADF imaging is commonly performed in parallel with EDX acquisitions. The corresponding chemical maps (Figure 12) depict the composition for the layered structure of the cross-section. As a main result, the tribofilm is shown to have molybdenum content in all parts.
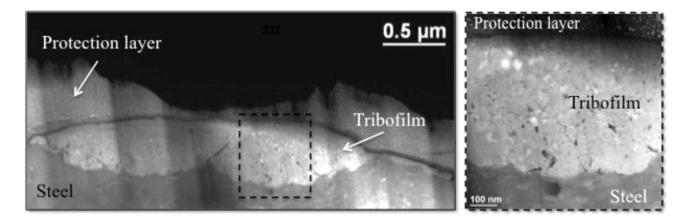

Fig. 11. HAADF images of tribofilm formed on the steel ball rubbed against an a-C:H:Si:O DLC coated flat coupon. (zoomed region on right).
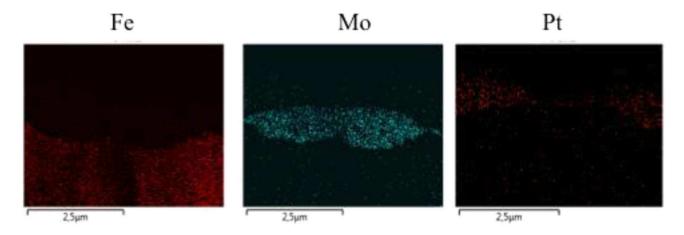

Fig. 12. TEM EDX mapping revealing the chemical composition of the structure of the tribofilm cross-section.

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Higher-magnification TEM images taken on this FIB cross-section (Figure 13) indicate that on the top part of the tribofilm, there is a heterogeneous extra layer. An EDX linear scan analysis shows that this thin layer is rich in titanium (Figure 14).

A selected-area electron diffraction (SAED) pattern (ca.250nm diameter) was obtained in the tribofilm material, as shown in Figure 15. The diffraction pattern obtained from the area shown in the inset is representative of a Debye-Scherrer type diffraction, where the diffraction rings are the result of numerous fine crystals lit up by the electron beam. It has been overlaid with the theoretical pattern of the MoC phase, having a face-centered cubic lattice (fcc), as identified in the JPDS file [22]. A good correlation is observed between the experimental SAED pattern of the tribofilm and the theoretical pattern for the MoC phase, clearly confirming the presence of MoC crystals. A bright-field (BF) image of the tribofilm (a) and a series of dark-field (DF) TEM images (b, c and d) are also shown in Figure 15. The TEM-DF cross-section images are obtained after a selection of a small part of the first two rings, so a small fraction of the crystalline grains appear bright. These images revealed a nano-crystalline structure for the tribofilm, with a carbide crystallite grain average size varying between ca.10nm and ca.60nm.
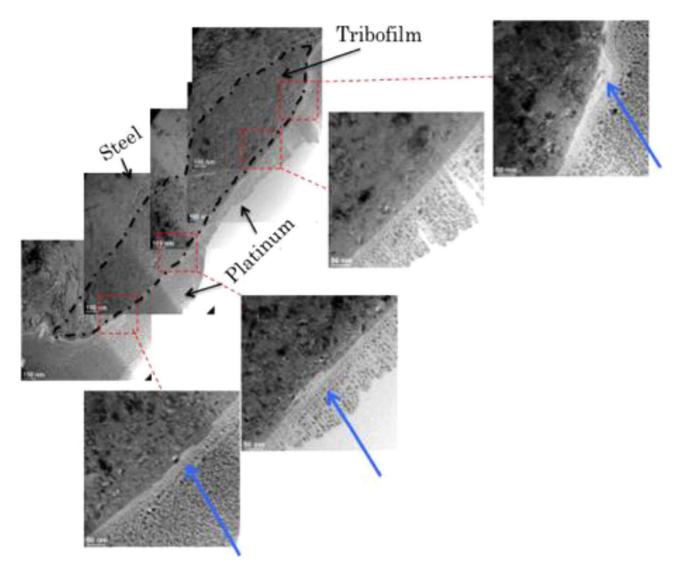
Fig. 13. TEM images for the tribofilm formed on the steel ball. A series of higher-resolution images are also shown. The blue arrows point to the extra-layer identified at the tribofilm/platinum interface (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Fig. 14. Molybdenum and titanium EDX line scans recorded across the tribofilm formed on the steel ball.

Fig. 15. SAED pattern for the area of the tribofilm shown in the inset. A bright-field image (a) and a series of dark-field images (b, c, d) performed on the tribofilm formed on the steel ball.

Table 2 displays the comparison between the theoretical and experimental numerical results for the d-spacing of the rings. This confirms that the electron diffraction pattern obtained can be directly interpretable as crystalline molybdenum carbide compounds.

N°	d _exp_ (nm)	d _CMo_ (nm)	{hkl}
1	0,2473	0,2472	111
2	0,2148	0,214	200
3	0,1507	0,1514	220
4	0,1285	0,1291	311
5	0,122	0,1236	222
6	0,1066	0,107	400
7	0,096	0,0982-0,0957	331-420
8	0,0866	0,0874	422
9	0,0815	0,0824	511
10	0,071	0,7135	333

Table 2. Experimental miller indices perfectly matching to the molybdenum carbide theoretical values (JPDS 03-065-8092).

An accurate analysis of the SAED pattern conducted on the tribofilm (Figure 16) revealed extra

spots, which can be interpreted as crystalline graphitic-based material.

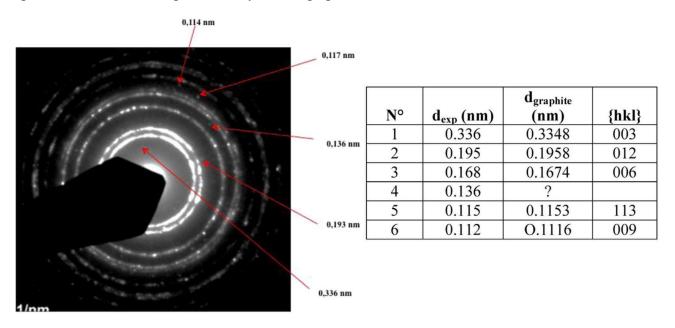| N°	d_{exp} (nm)	$d_{graphite}$ (nm)	{hkl}
1	0.336	0.3348	003
2	0.195	0.1958	012
3	0.168	0.1674	006
4	0.136	?	
5	0.115	0.1153	113
6	0.112	O.1116	009

Fig. 16. SAED pattern of the tribofilm showing the extra spots present in the pattern (a). Some experimental Miller indices may match the graphite theoretical values (JCPDS 00-026-1079)(b).

In fact, comparing the approximate experimental and theoretical (JCPDS00-026-1079) values for

the d-spacing of the rings (Table in Figure 16) it can be clearly seen that there is good matching

between the structure present inside the tribofilm and the graphitic-based material (even if it is in a much smaller amount in comparison to the MoC species).

A high-resolution TEM micrograph of an isolated grain is shown in Figure 17. The fringes in the image and the corresponding spots in the Fourier transform (inset in Figure 17) confirm that the tribofilm formed on the steel ball has a crystalline structure and that the inter-reticular distances (Table 3) match those of the MoC compound, as previously given. However, the angles of the reticular planes do not match perfectly with an fcc lattice. This could be explained by considering some crystal deformations as a result of internal stresses or by supposing that there is a specific super-position of two crystals of MoC.
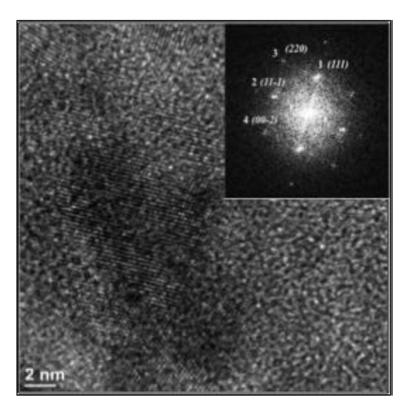

Fig. 17. High-resolution TEM image recorded on the tribofilm formed on the steel ball during the tribotest. In the inset is the indexed Fast Fourier Transform (FFT) of the micrograph.

N°	d $_{exp}$ (nm)	d $_{Graphite}$ (nm)	{hkl}	Angles$_{(exp)}$	Angles$_{(theory)}$
1	0,248	0,2472	111	0°	0°
2	0,239	0,2472	111	78.8°	70.5°
3	0,157	0,151	220	39.5°	35.3°
4	0,200	0,214	200	126.7°	125.3°

Table 3. Comparison between experimental and theoretical interreticular distances and angles of MoC (JCPDS 03-065-8092).

3.3.3. Nano-indentation

Molybdenum carbide is widely used for cutting tools and abrasive materials [23, 24] due to its high hardness (15.5–24.5 GPa) [25]. For this reason, nano-indentation has been employed to evaluate the mechanical properties of the MoC-containing tribofilm formed on the steel ball in order to know if abrasive wear should be taken into consideration during the observed wear process. Figure 18 shows the hardness of the different zones identified on the tribofilm. For each indentation performed, the sample was imaged after the test (Figures 18a, 18b, 18c).
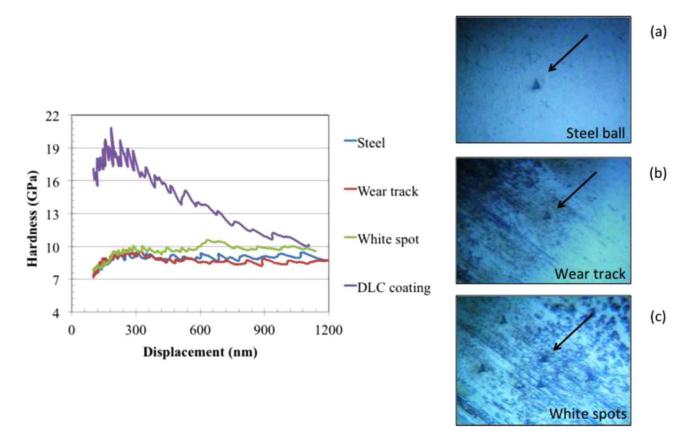

Fig. 18. Nano-indentation curves for the selected areas: steel substrate (a), wear track (b) and white spots (c).

The values obtained in the 200 nm displacement zone are assumed to be representative of the hardness for the DLC analysed (19 GPa) and the 100C6 steel substrate used (8–10 GPa). It may be observed that the DLC coating is stiffer than both the MoC-containing tribofilm (white spot – ~ 10 GPa) and the standard heat-treated 100C6 steel substrate (62 HRC = approximately 10 GPa). These findings suggest that the wear produced on the DLC-coated flat coupon cannot be considered abrasive wear.

3.4. Tribological behaviour of DLC/DLC tribo-pairs in the presence of MoDTC

To study the catalytic role of the steel in the DLC wear mechanisms, the DLC/DLC tribo-pair configuration has been tested. The friction coefficient versus time curves obtained in the presence of base oil alone and with MoDTC-containing base oil are plotted in Figure 19(a). The base oil gave relatively high friction coefficient, approximately 0.12, a value similar to those obtained for the steel/steel and steel/DLC configurations. However, blending 1% in wt. of MoDTC into the base oil leads to a consistent reduction in friction. In this case, the wear produced on the silicon-doped DLC-coated flat coupon (Figure 19(b)) is much less significant (track width 150 μm while Hertzian diameter is140 μm) than that in the previous steel/DLC configuration.
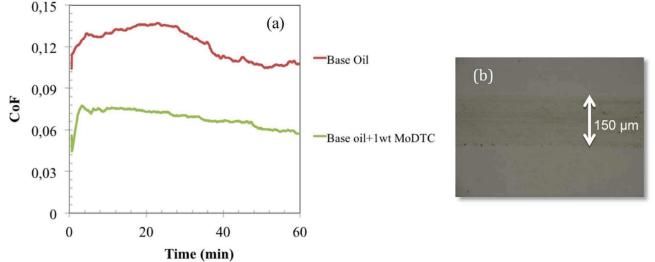

Fig. 19. (a) Friction behaviour of silicon-doped DLC/DLC tribo-pair configuration lubricated by MoDTC-containing base oil. (b) Friction wear track on the silicon-doped DLC flat coupon.

4. Discussions

A complementary multi-technique approach provides valuable insights into the mechanisms underlying the new proposed wear model for the DLC coating when lubricated by MoDTC-containing oil. According to our XPS analysis and the TEM characterizations, it is possible to accurately depict the multi-layer structure of the DLC coating studied in this work as in Figure 20.
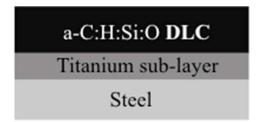

Fig. 20. DLC multi-layer structure

It was important to confirm the presence of Si-C bonds on the DLC top surface. In fact, in some studies [23, 26], silicon-doped coatings are believed to have two different networks, silica and carbon-based. In particular, it has been reported that the amorphous structure containing a mixture of sp^2 and sp^3 bonds is interpenetrated with the SiO_2 network [23, 26]. The results shown in the previous sections demonstrate that the DLC coating studied in this work presents a complicated network, formed by carbon, hydrogen, silicon and oxygen atoms, thus also containing Si-C bonds in all the whole thickness of the network.

Afterwards, a deeper characterization of the tribofilm formed on the steel ball that was slid against the DLC-coated flat coupon was performed. Energy Dispersive X-ray (EDX) spectroscopy analysis confirmed the presence of molybdenum-based compounds all over the tribofilm. The investigation of the tribofilm with HR-TEM and SAED clearly suggests the growth of a multi-phase tribofilm containing MoC species in a matrix made of carbon and relative small amounts of molybdenum sulfide and molybdenum oxide species. Considering the good correlation between the experimental

data and the corresponding JCPDS file, the presence of the fcc Mo-C species in the relatively thick and continuous tribofilm formed on the steel ball is noted. This has also been confirmed by means of the SAED diffraction pattern analysis performed on a single crystal. The molybdenum carbide crystallites display a face-centered cubic structure and, employing dark-field images (Figure 15), it is possible to individuate the grain size varying between 5 nm and 60 nm.

In the HR-TEM images shown in Figure 13, there was observed the presence of an extra thin and heterogeneous layer. Surprisingly, EDX line scan experiments conducted on the tribofilm/platinum interphase revealed titanium as the main component. This could be explained by supposing that the removal of DLC from the coated coupon onto the steel ball is so catastrophic in some places that it causes even the transfer of some of the titanium sub-layer after the complete removal of the DLC material.

The comparison between the tribofilm and the DLC hardness to the steel substrate value is used to determine if the stiffness of the carbide tribofilm can produce abrasive wear of the DLC coating.

The dark grey zone (wear track) and the white spots (carbide tribofilm shown in Figure 11) exhibit hardness comparable to that of the steel substrate. For this reason, the enhanced hardness value measured for the DLC coating suggests that the abrasive wear should not be taken into account as the principal wear mechanism.

The results shown in this paper validate the hypothesis that the tribofilm was generated by a chemical reaction between the molybdenum atoms adsorbed on the steel ball and the dangling carbon generated on the DLC coating after the Si-C breaking.

However, an alternative pathway involving the hydrogenated-DLC as a carburizing reagent can be proposed. Based on the work of Wang et al. [27] on the synthesis of molybdenum carbides, direct carburization of MoO_3 by C_2H_6/H_2 gas mixture produces MoC_x with excess graphitic carbon. This could be proved by investigating hydrogen-free carbon coatings and showing that they are less sensitive to chemical wear by MoDTC.

These findings allow the authors to propose, for the first time, a multi-step wear model, schematized in Figure 21. $MoS_{2-x}O_x$ compounds are supposed to form first on the steel counterface. (Molybdenum-based tribofilm). Then Si–C bonds of the Si-doped DLC break because of friction. Subsequently, Molybdenum contained inside the tribofilm on the steel ball may react with C dangling bond generated on the DLC, resulting in molybdenum carbide generation in a matrix of Mo-O-Fe-S compounds. In particular, it has been confirmed that the principal cause of the wearing out of DLC when lubricated with MoDTC is the formation of molybdenum carbide crystallites on the steel ball that slides against a-C:H:Si:O DLC. The key role of steel in the wear mechanism has also been demonstrated. In fact, the test performed using the DLC/DLC configuration gave better friction reduction, and much lower wear was obtained on the DLC. In this case, no molybdenum carbide compound was detected on the rubbed surfaces.

In addition, it could be interesting to investigate the effect of the Si dopant introduction into the amorphous DLC network on this carburizing process.

As said before, it is important to perform further analysis to determine whether the hybridization change of carbon onto the DLC plays a key role in accelerating the coating failure mechanisms. This complementary aspect will be the central core of another paper.
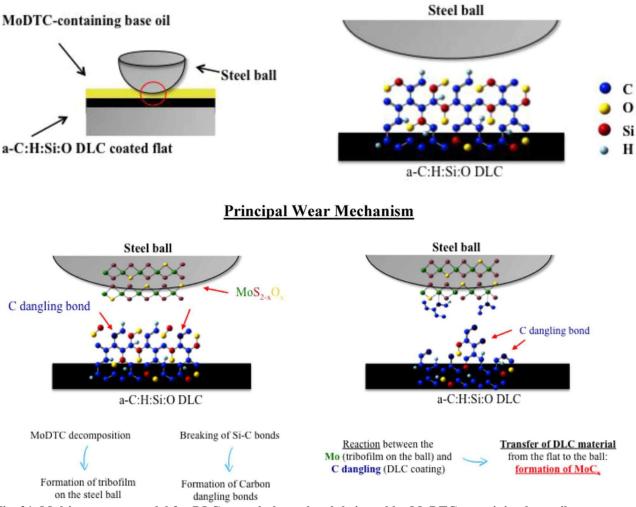
Initial situation

Principal Wear Mechanism

Fig. 21. Multi-step wear model for DLC-coated plate when lubricated by MoDTC-containing base oil.

5. Conclusion

To gain insight into the drastic DLC wear induced by MoDTC lubrication, post-mortem analyses have been performed on both steel and DLC surfaces, and the following findings have been obtained.

– The presence of molybdenum carbide (MoC) on the steel counterpart that was slid against silicon-doped DLC has been evidenced both by XPS and by the TEM/EDX analysis of FIB cross-section samples. Important understandings were obtained through crystallographic studies where a

nanocrystalline structure of carbides are displayed. Importantly, there is no carbide on the DLC counterface.

– A possible role of abrasion of the DLC by the hard carbide-based tribofilm has been discussed. Tribofilm hardness values were obtained from the nano-indentation curves. Considering that the tribofilm's mechanical properties are quite close to those of the steel substrate, this strongly suggests that the abrasion wear mechanism is not predominant. Moreover the small size of MoC nanoparticles embedded in the tribofilm is not in favour of a two-body abrasion process.

– Therefore, all the data are in agreement with a chemical wear mechanism.

Although the exactly steps order of the wear mechanism remains unclear, these results might be helpful in developing a new MoDTC-containing lubricant (considering interactions with other additives) and a different DLC composition or structure compatible with the MoDTC friction modifier.

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