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MoDTC tribochemistry in steel/steel and steel/DLC systems lubricated with model lubricants and fully formulated engine oils.

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Abstract

This work focuses on the tribochemistry of molybdenum dithiocarbamate (MoDTC) oil additive to improve friction behavior of DLC coated systems lubricated in boundary regime. Raman microscopy has been used to investigate surface tribolayers formed on coated and steel surfaces when lubricated with model lubricant and commercial engine oils. The effect of oil additives and the type of DLC played a crucial role in the development and composition of the tribolayer and the friction performance. For the first time, it is shown that a distinctive MoS_2-containing tribolayer can be formed on the ta-C surface, leading to a coefficient of friction lower than 0.04. The underlying mechanisms of MoDTC/surface interactions and their effect on friction and wear are discussed.

Keywords: DLC, Molybdenum dithiocarbamate (MoDTC), Raman spectroscopy, boundary lubrication

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1. Introduction

One of the main targets in engine oil development is to increase fuel efficiency by means of reducing friction losses in tribological contacts. To achieve this goal, the general trend is to adopt oils with low viscosity, as significant frictional losses in the engine occur in systems where components in contact run in the hydrodynamic lubrication regime. This trend is supported by the introduction of new standards that require using lower viscosity oils to satisfy the needs of OEMs [1]. However, reducing the oil viscosity will result in several tribological systems being run into the boundary and mixed lubrication regime, resulting not only in increased friction, but also in excessive wear, compromising the engine durability.

A good approach is to keep low viscosity in the oil, reducing the friction in tribological systems under the hydrodynamic regime (i.e. crankshaft/main bearing accounting 25% of friction losses [2]); and by using specific engine oil additives to reduce friction and control wear in systems working in boundary and mixed regime (i.e. cam/follower, piston/liner at Top Dead Centre and Bottom Dead Centre) [3, 4]. Some of these oil additives are known as friction modifiers (FM). Different chemistries, such as organic polar molecules, functionalised polymers and organic molybdenum compounds can be used as friction modifiers. Among these additives, molybdenum dithiocarbamate (MoDTC) has been demonstrated to be a very efficient FM additive, leading towards low friction values under several conditions [5-8]. It is well established that MoDTC under certain tribological conditions produces MoS_2 on the surfaces. MoS_2 is an excellent solid lubricant, which reduces friction due to its layered crystalline structure with weak bonds between laminar sheets [9-11].

OEMs are increasingly manufacturing components with hard coatings to enhance tribological properties. However, their behavior in boundary-lubricated contacts is still not well-understood. For standard engine applications, diamond-like-carbon (DLC) coatings are the material of choice, due to high wear resistance, low friction and a natural inertness that prevents surface corrosion [12-14]. Several publications discuss the role of MoDTC in both steel and DLC systems under different testing conditions [6, 7, 15-17]. Temperature, additive concentration, contact pressure, roughness, slide/rolling ratio, stroke, etc. play a role in the performance of this additive. Surface materials are also crucial in the development of a friction reducing tribolayer. Different tribochemistry mechanisms have been proposed depending on the lubricant, coating and the testing conditions [18].

In addition to MoDTC interactions with the surface, MoDTC interactions with other additives in the oil are very important for its performance as a friction modifier. There is a consensus about the synergistic effect of MoDTC with antiwear additive zinc dialkyldithiophosphate (ZDDP) in both base oils and fully-formulated oils [19]. However, interactions between MoDTC and other common engine oil additives, like detergents or dispersants, are much less understood. Some studies reported a positive detergent/dispersant interaction with MoDTC [20, 21], whereas negative effects were identified in others studies [22, 23].

The main aim of the current study is to understand the effect of an anti-wear/detergents/dispersants/anti-oxidant additive package on MoDTC tribolayer formation on ferrous and coated surfaces, and its impact on tribological performance.

2. Experimental

Additive tribolayer formation ability and tribological performance have been studied in a benchtop tribometer, while the tribolayers formed have been characterized using Raman spectroscopy. This technique has already been proved as the tool of choice for MoS_2 analysis [24, 25], as it can easily determine and distinguish the presence of several molybdenum based chemical compounds in the tribolayer.

2.1. Test rig

A pin-on-disk tribometer was used to provide a unidirectional pure sliding point/flat contact, simulating a boundary lubricated contact. The schematic representation of the contact in the rig is shown in **Figure 1**. A stationary ball was used as the pin part, whereas a washer fixed to a spindle was used as the rotating disk. A static load was provided by applying a dead weight.

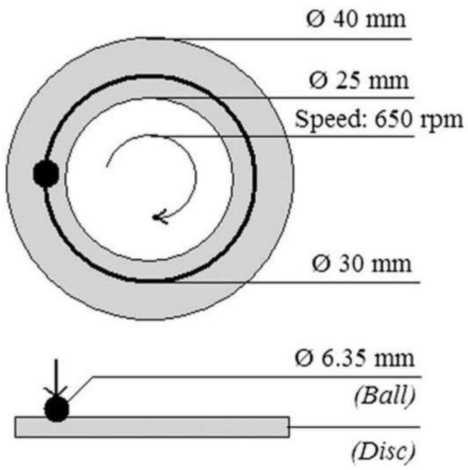


Figure 1. The schematic of the tribometer and dimensions of pin-on-disk parts

Friction force was measured in real-time throughout the entire test using a load cell with 0.02 N total error and recorded using a data acquisition system connected to a PC. Sampled data were averaged every second.

2.2. Test conditions

The testing conditions are shown in **Table 1**. The test duration was two hours, equivalent to 7344 m of sliding distance. A lubricant temperature of 100 °C was set. An initial contact pressure, calculated from Hertzian initial point contact, of 1 GPa was applied for the tests with coated and uncoated samples. At least three tests were performed for every set of conditions to ensure repeatability of friction and wear results.

Film thickness was calculated using Dowson and Hamrock equation for point to flat contact [26]. The initial lambda ratio obtained is less than one, confirming that the tests were performed in boundary lubrication regime.

Due to the very low wear obtained, the wear volume could be accurately measured only on the steel ball. The wear volume was determined by measuring the ball wear scar diameter and calculating the sphere cap worn out. The ball wear scar diameter was obtained using the optical microscope and the wear volume was obtained using the equation:

$$V_{wear} = \frac{\pi h(3r^2 + h^2)}{6}$$

Where $h = R - \sqrt{R^2 - r^2}$, being h the height of the cap removed, R the radius of the ball, and r the radius of the circular wear scar.

Table 1. Experimental conditions.

Initial contact pressure	1 GPa
Temperature	100 °C
Sliding speed	1.02 m/s
Test duration	2 h
Film thickness ratio	<0.031 Boundary lubrication regime

2.3. Materials and lubricants

Three different material pairs were used: steel/steel, steel/a-C:H and steel/ta-C. The coatings were selected with the aim to assess the role of hydrogen on the tribolayer formation and tribological performance. Both these coatings are of interest to OEM industry and they are being introduced in several engine components such as tappets, gudgeon pins and piston rings [27]. The material for the ball was AISI 52100 high chromium bearing steel, whereas the steel disk consisted of AISI 1050 medium carbon steel, quenched and tempered. The hydrogenated amorphous DLC (namely a-C:H) consists of a plasma-assisted chemical vapor deposition 1µm-thick coating, containing 25-30% hydrogen applied on the disk with a SiOC interlayer. The non-hydrogenated tetrahedral amorphous coating (ta-C) comprises a 150 nm coating deposited using physical vapor deposition applied on the AISI 1050 disks with a Cr sublayer. A Nanotest Platform 3 by Nanomaterials (Wrexham, UK) was used to measure the coating hardness and modulus. A load cycle was applied at a speed of 0.5 mN/s for both loading and unloading ramps, with an initial load of 0.01 mN and a maximum load of 20 mN. Roughness was measured using a Talysurf 120L contact profilometer

(Taylor-Hobson, Leicester, UK) with 2 µm conical shaped diamond stylus. Relevant properties for the samples used in this study are summarised in **Table 2**.

Table 2. Mechanical properties.

Sample	Material	Method	Thickness	% H	% sp^3	Hardness	E	R_q (µm)
Ball	AISI 52100	-	-	-	-	64 HRC	210 GPa	0.0046
Disks								
steel	AISI 1050	-	-	-	-	60 HRC	210 GPa	0.307
a-C:H		PACVD	1 µm	25-30	40-55	12.3 GPa	107 GPa	0.219
ta-C		PVD	0.15 µm	< 0.5	> 60	28.5 GPa	201 GPa	0.359

To assess the interactions and tribochemistry of molybdenum based additives, several lubricants were blended and tested. A group III oil as a basestock, and its correspondent SAE 5W30 fully-formulated oil were used. The fully-formulated lubricant consisted of a basestock, viscosity improver, 1% ZDDP antiwear and an additive package containing antioxidants, detergents and dispersants. The MoDTC additive (generic structure presented in **Figure 2**) was added to both the base oil and the fully-formulated oil in a 0.5 wt% to achieve a proportion of 500 ppm Mo in the oil. A list of the lubricants used in this work is presented in **Table 3**.

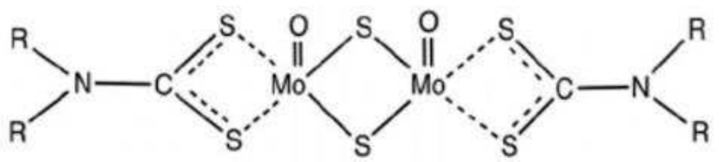


Figure 2. MoDTC additive structure.

Table 3. Lubricants blended and designation.

Group III basestock	BO
Group III basestock + MoDTC	BO+MoDTC
Fully formulated oil	FF
Fully formulated oil + MoDTC	FF+MoDTC

2.4. Surface analysis

To determine the formation of low friction MoS_2 tribolayers on the tested surfaces, the Raman microscopy was performed using an in-Via Renishaw system (Renishaw plc., Gloucestershire, UK), with a 488 nm laser excitation source, 2400 lines/mm grating and a Peltier cooled CCD detector providing a spectral resolution of 1 cm^{-1}. This spectrometer operates in combination with a Leica optical microscope using a 50x objective lens in backscattering mode, providing a lateral resolution of 1 µm. Disks and balls were rinsed with heptane to remove the excessive lubricant in order to avoid lubricant-related fluorescence during the Raman analysis.

3. Results and discussion

3.1. Friction

Figure 3 shows the average friction from the last hour of the test. In general, MoDTC blended in base oil leads to lower friction compared to base oil alone in lubricated tests. When MoDTC was added in the FF oil, friction performance of the steel/steel contact was seen to only slightly improve.

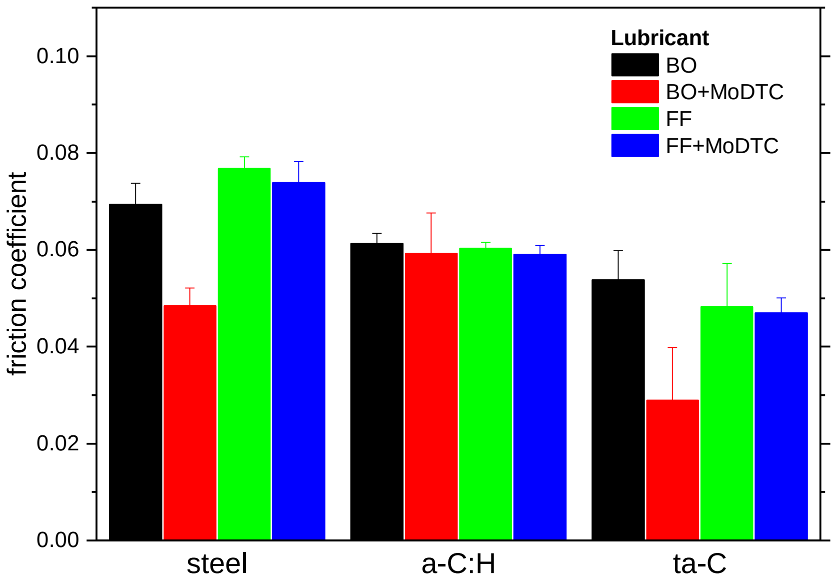


Figure 3. Average steady-state friction for all the material-lubricant combinations used in this study.

Friction in steel/DLC systems was generally low, and for the steel/a-C:H contact, not significantly affected by the lubricant used. A key observation was the significant friction reduction when testing the ta-C coating with the BO+MoDTC lubricant. Friction reduction of steel/DLC systems with respect to the steel/steel system, could be partially attributed to high wear of the ball counterpart. With wear the contact becomes more conformational, potentially leading to a change in the lubrication regime from boundary to mixed/full film regime. On the other hand, DLC has an inherent low coefficient of friction in comparison to steel systems, due to the role of carbon structural changes and the formation of a transfer layer [28-34]. The mechanisms of friction reduction are discussed below, based on the friction evolution with time, wear and tribolayer chemical composition.

Figure 4 presents the friction coefficient throughout the whole test. When the BO+MoDTC lubricant was used in the steel/steel tests (**Figure 4a),** a sharp decrease in friction after around 10 minutes test was observed. In contrast, adding MoDTC to fully-formulated oil resulted in low friction from the start of the test. This low friction was then gradually lost during the test.

Regarding the steel/a-C:H contact (**Figure 4b**), a different performance was observed. In this case, no differences between oils exist in the steady-state regime. There is only a very strong reduction in friction in the initial stages of BO+MoDTC test, which could be attributed to MoS_2 and DLC synergistic effect, but this very low friction situation was not sustained in time. This effect has been reported by DeFeo et al. using steel/Si-DLC, claiming it occurred due to the formation of MoS_xO_y on the steel counterpart [35]. Eventually, all the additives yielded the same coefficient of friction in the long term.

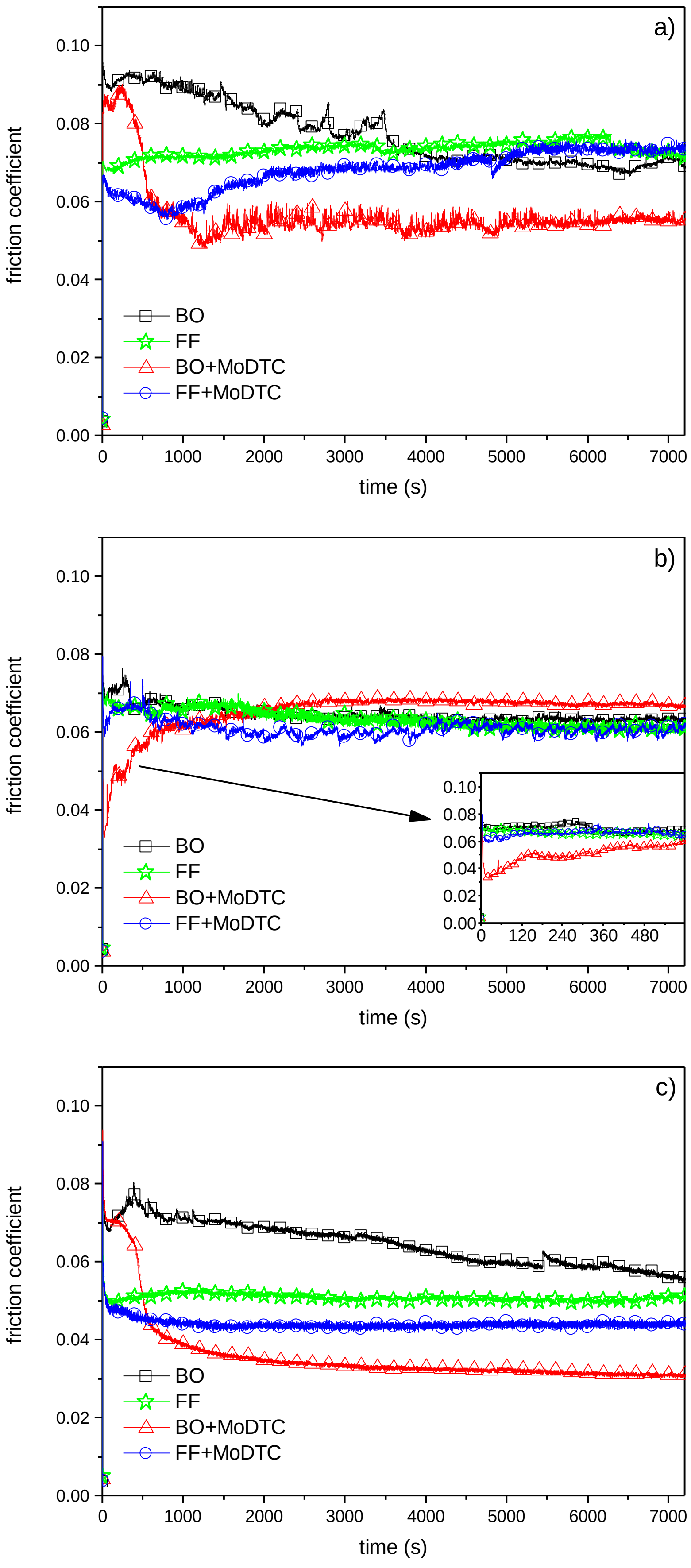


Figure 4. Friction coefficient vs sliding time in a) steel/steel b) steel/a-C:H and c) steel/ta-C contacts.

In relation to the harder non-hydrogenated ta-C coating (**Figure 4c**), a low friction performance was achieved. These low friction values are consistent with the data reported by other groups in steel/ta-C [34, 36, 37] and ta-C/ta-C contacts [34, 38]. When BO+MoDTC was used, a strong friction reduction is achieved after a few minutes, providing a very low coefficient of friction (<0.04). When MoDTC is blended in FF oil, no friction reduction was achieved with respect to non-molybdenum-containing FF oil lubricated contact. Similar performance is found in other works involving DLC and fully-formulated oils containing MoDTC [39-42], where no additional frictional reduction was obtained when MoDTC was blended into a FF oil with respect to the results corresponding to the non MoDTC-containing FF oils.

3.2. Wear

Because of very low wear values, only the wear on steel balls was measurable. There is one exception regarding the disks, which is a-C:H coated disk tested against steel ball with the BO+MoDTC lubricant. **Figure 5** shows wear coefficient for all the material/lubricant combinations tested in this study.

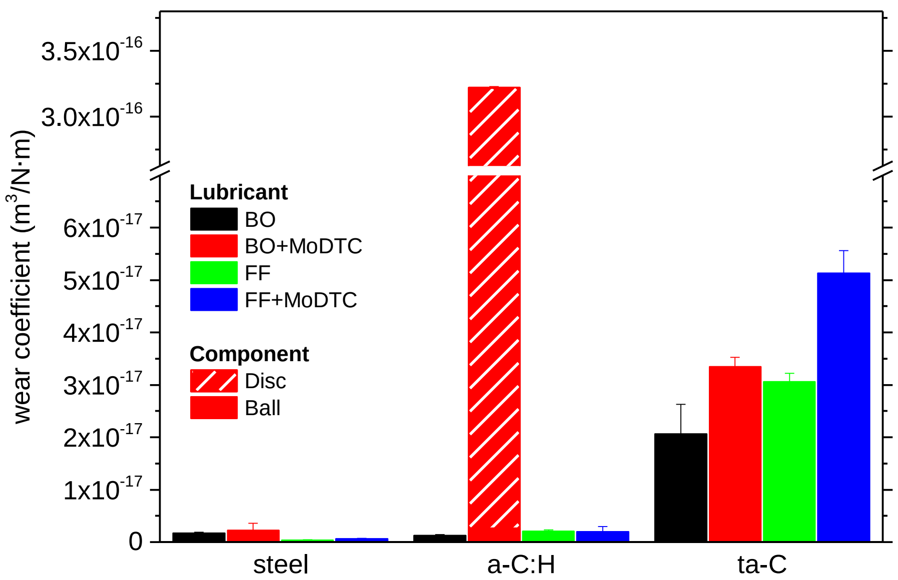


Figure 5. Wear coefficient for all the material-lubricant combinations used in this study. The dashed bars represent the disk wear. Disk wear was measurable only for the a-C:H disk when lubricated with BO+MoDTC lubricant.

Generally speaking, wear coefficient is low, below $1x10^{-16}$ m^3/Nm. Lowest wear values are found for the steel/steel tribopairs tested with ZDDP-containing lubricants, due to the effective antiwear tribolayer formed on the surfaces.

The high steel ball wear in steel/ta-C tests, reported before in similar material systems [43-45], is thought to be due to the difference in materials hardness. The higher hardness of the ta-C coating (28.5 GPa) leads to accelerated wear of the lower hardness steel counterface (60 HRC).

Figure 6 shows the optical microscope images obtained from the wear scar on disks. These images were then analyzed to evaluate qualitatively the damage level on the disk as well as to determine the presence of a tribolayer.

On steel disks, a 350 µm wear track is observed when using BO and BO+MoDTC. This width is larger than the calculated Hertzian stress diameter (90 µm), suggesting that there is still boundary contact after the initial running-in period. When using the FF lubricant in steel/steel systems, the wear track width is reduced by half, most probably due to the formation of anti-wear phosphate tribolayer from the ZDDP antiwear additive present in this lubricant. Disk wear behavior is different when hard DLC coatings are involved. In a-C:H coatings, non-measurable wear is observed when using BO, manifested by the presence of slight abrasion lines. When MoDTC is added to the base oil, however, a distinctive wear track is observed in a-C:H coating. In the ta-C coated disk, on the other hand, a stable tribolayer is formed on the surface, with some debris deposited on both sides of the wear track. No signs of wear or tribolayer were found in a-C:H or ta-C disks when FF oils are used, even when MoDTC was included in the blend. It is clear that in these cases, additives have played an important role restraining the degradation process of the coating and the tribolayer formation on the DLC coating.

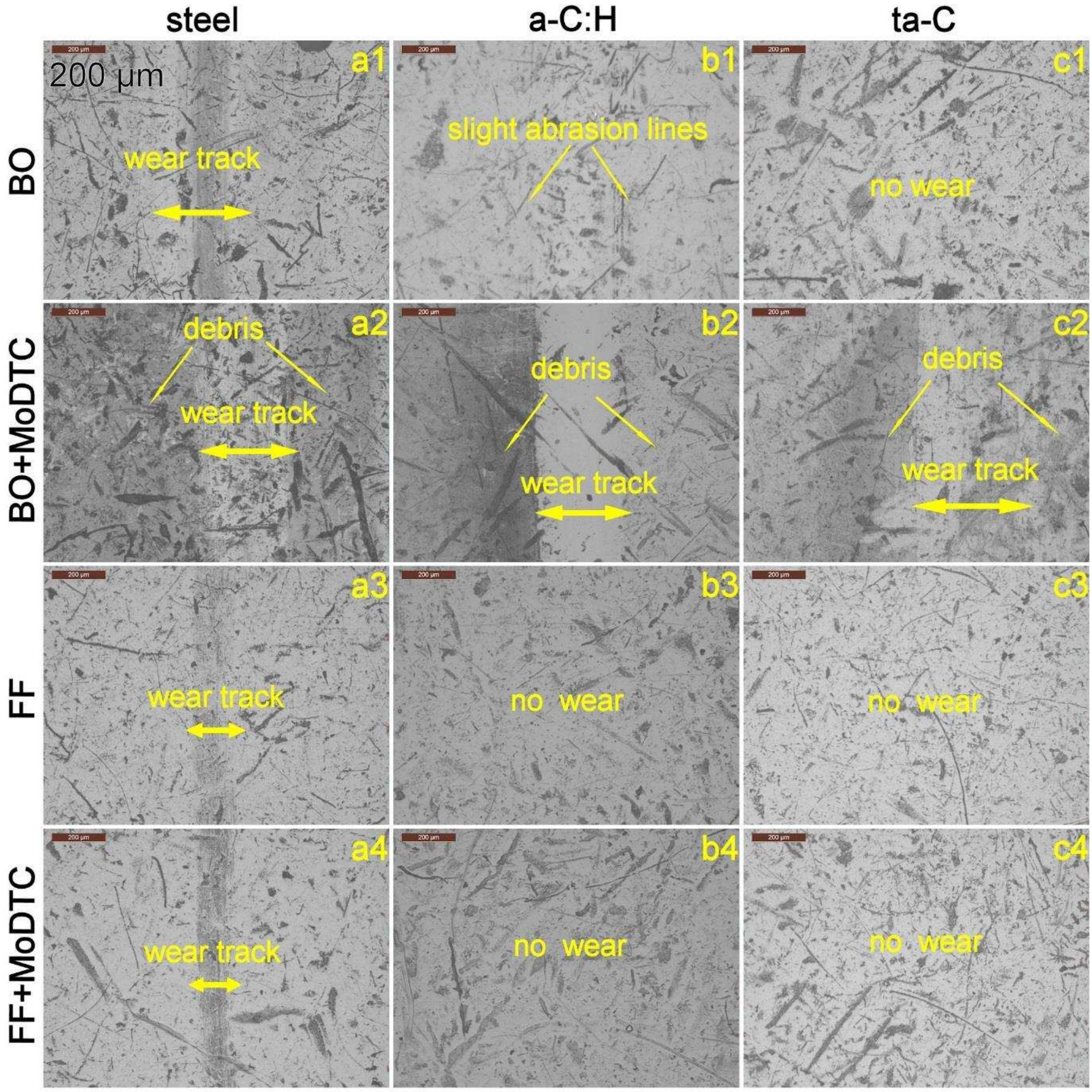


Figure 6. Disk wear track micrographs.

To support wear assessment on the disk samples, contact profilometry was carried out on the disks wear tracks in the transverse direction. No wear scar or changes in roughness could be determined except for the BO+MoDTC lubricated steel/a-C:H test, where a large wear track could be identified. High a-C:H coating wear when lubricated with a MoDTC containing lubricant has been reported in the literature by several groups. However, the mechanism of this performance is still not fully understood. First theories about higher wear track in DLC/ferrous alloy contacts [15, 31] in the presence of MoDTC hypothesize that the formation of hard molybdenum oxides from MoDTC are the reason. Other authors point out that MoS_2 enhances the graphitisation process in

DLC coatings [46, 47] through a precursor stage involving hydrogen evolution and sp^3 structure destabilization, promoting the formation of a brittle graphitic sp^2 structure [48]. More recent works by De Feo et al. [49] indicate that sequestration of C from the Si–C bond leads to the formation of Mo_xC and as a result, to high coating wear. On the other hand, Okubo and Sasaki [50] remark the formation of hard molybdenum carbides that contribute to DLC degradation. Interestingly, no wear track could be observed in a-C:H coating when molybdenum is blended into a fully-formulated oil, as seen in **Figure 7**.

As for the ta-C coating, no distinctive wear was obtained when using the BO+MoDTC lubricant. This result agrees with the findings reported by Masuko et al. [51], indicating that excessive wear on DLC in the presence of molybdenum-containing additives does not occur when hydrogen content in the coating is 10% or less.

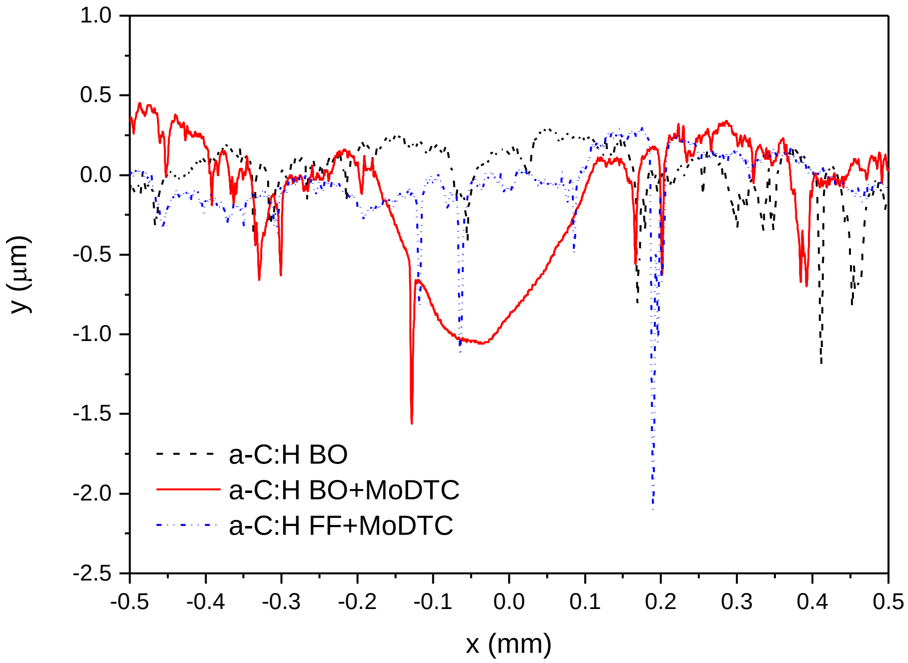


Figure 7. Contact profilometry on a-C:H coated disk samples tested using BO, BO+MoDTC and FF+MoDTC lubricants.

3.3. Surface analysis

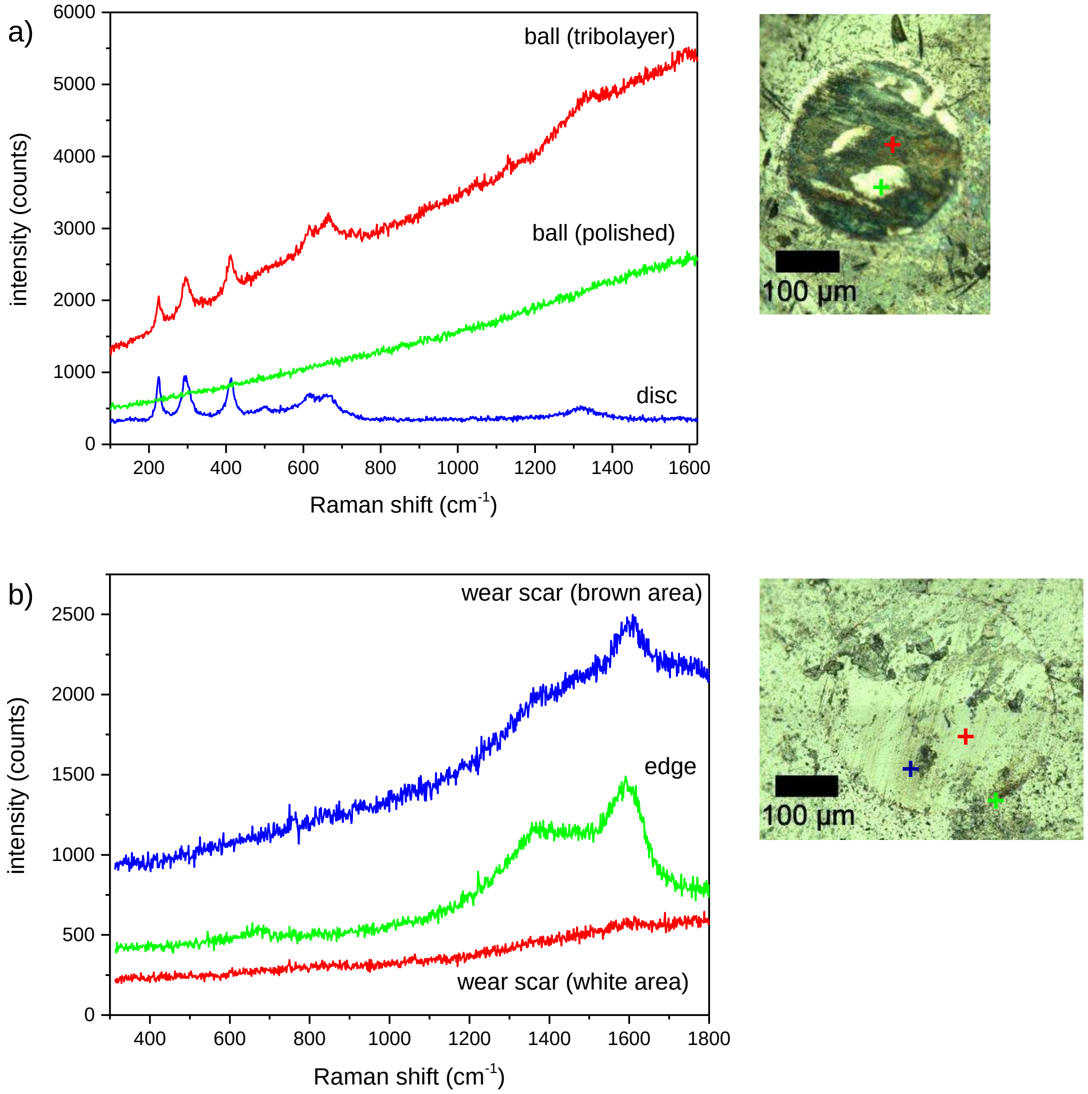
To resolve the differences between steel and coated systems, surface analyses using Raman microscopy were carried out. For steel/coated contacts, both the ball and the disk were analyzed using Raman microscopy due to the different nature of the surfaces. **Table 4** summarizes the main chemical species detected with Raman microscopy on the ball and disk wear scar.

Table 4. Steel/steel and steel/coated systems wear scar chemical composition.

	steel/steel	steel/a-C:H	steel/ta-C
BO	Ball: Oxides.	Ball: No Oxides. Carbonaceous species.	Ball: Oxides. Carbonaceous species at the edge.
	Disk: Oxides.	N.A.	N.A.
FF	Ball: No oxides. Fluorescence.	Ball: No oxides. Fluorescence.	Ball: No oxides. Fluorescence.
	Disk: No oxides. Fluorescence.	N.A.	N.A.
BO+MoDTC	Ball: MoS_2 distributed in all the tribolayer. Strong signal.	Ball: MoS_2 in steel ball (patchy). Carbonaceous species.	Ball: MoS_2 in steel ball (patchy).
	Disk: MoS_2 distributed in all the tribolayer. Strong signal.	Disk: MoS_2 in the edge of wear track. No MoS_2 inside the wear track.	Disk: MoS_2 in DLC tribolayer (patchy).
FF+MoDTC	Ball: No oxides. Fluorescence.	Ball: MoS_2 found in the ball (patchy). Fluorescence.	Ball: Carbonaceous species at the edge.
	Disk: No oxides. Fluorescence.	N.A.	N.A.

3.3.1. Base oil lubricated tests

Figure 8a shows the Raman spectra obtained from the BO tested steel/steel system. Peaks corresponding to hematite (Fe_2O_3) (peaks at 225, 290-300, 405 and 1320 cm^{-1}) are detected on the tribolayer, as well as magnetite (Fe_3O_4) revealed by the 660 cm^{-1} peak [52, 53]. Some polished areas in the ball wear scar show no Raman sensitive chemical compounds, confirming the absence of oxides in these areas. When analyzing the steel/a-C:H wear scars on the ball and disk (**Figure 8b**), only carbonaceous deposits could be detected. No oxides were detected. The spectra of the carbonaceous material are similar to the polymeric a-C:H characteristic baseline D, G peaks [54]. This type of graphitized transfer layer is found on counterfaces (steel, Si_3N_4) for DLC/other material tribological systems [30, 55, 56]. As for ta-C coating, shown in **Figure 8c**, a mixture of iron oxides (both hematite and magnetite) and amorphous carbon (broad peaks at 1350 and 1600 cm^{-1}) are found on the entire wear scar. In this case, at the edge of the wear scar, there seems to be a more extensive carbonaceous transfer layer than in the inner part of the wear scar. This carbonaceous layer formed on top of the ball is much smaller than the one transferred from the more reactive a-C:H surface, and it approximately matches the carbon signal found in the steel/steel system. Thus, the presence of the carbon material in this case seems to come from the lubricant, rather than from the DLC counterface.



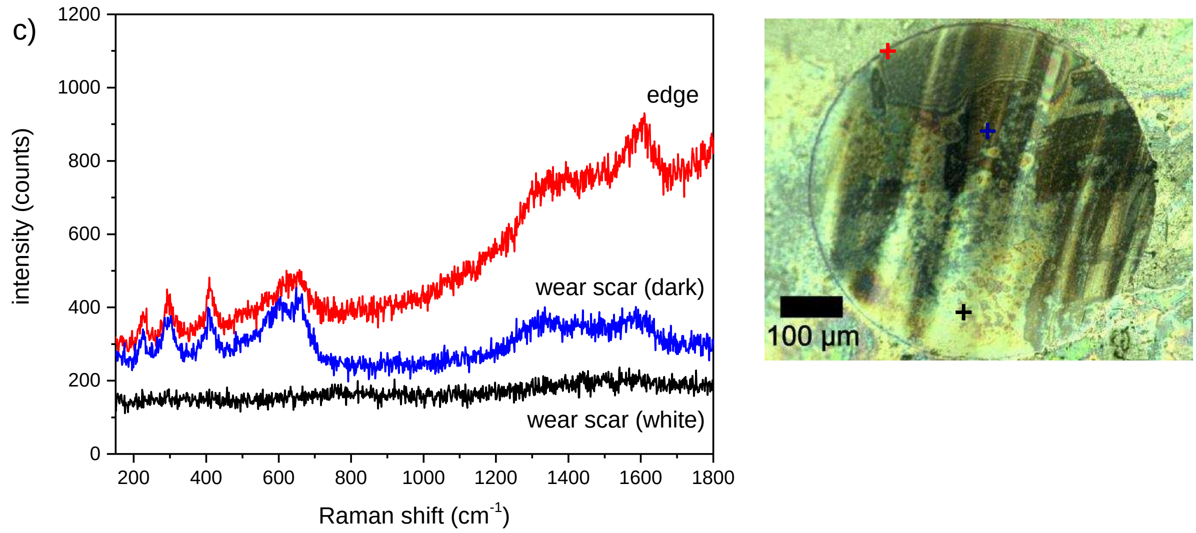


Figure 8. Raman microscopy on different surfaces tested using BO as a lubricant: a) steel/steel, b) steel/a-C:H, c) steel/ta-C.

3.3.2. Base oil with MoDTC lubricated tests

Stronger differences depending on the material pair were found when using BO+MoDTC lubricant. In steel/steel contact, Raman spectra (**Figure 9a)** show the two characteristic peaks at 379 and 410 cm^{-1} [57, 58], confirming that the MoS_2 is distributed on the entire wear scar [59]. Also, the debris produced in the contact is seen to collect around the ball wear scar, showing carbon-related peaks (D and G broad bands at 1350 and 1600 cm^{-1}). On the other hand, MoS_2 distribution varies across the disk wear scar, being higher on the outside than in the center of the wear scar (see **Figure 9b**). Similarly to the ball, carbon features are more noticeable in the debris than in the center of the wear scar.

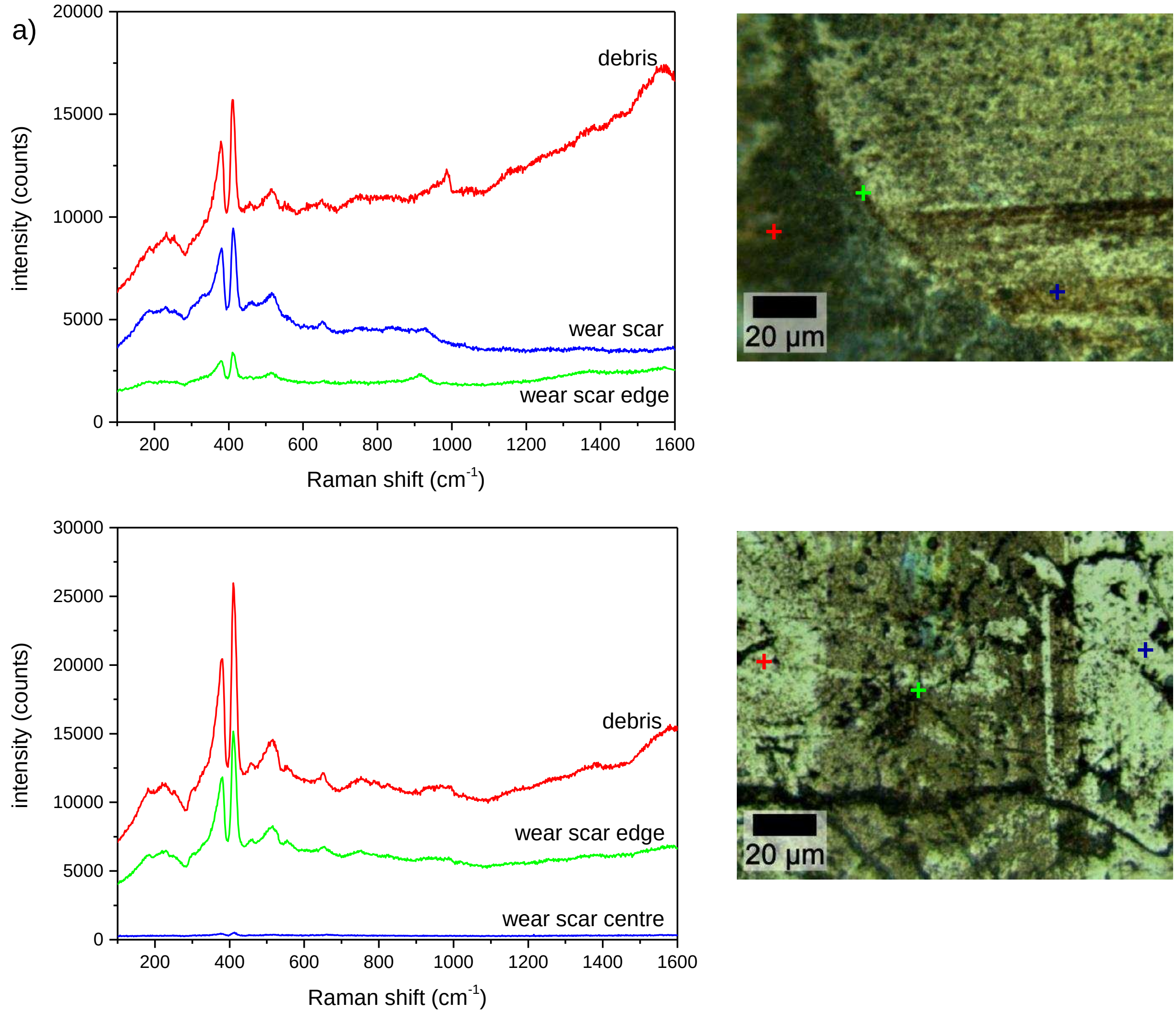


Figure 9. Raman analysis of a) steel ball, and b) steel disk, in BO+MoDTC lubricated test.

In steel/a-C:H contact lubricated with BO+MoDTC, the a-C:H sample exhibits a large level of degradation and visible wear debris at both sides of the wear track. Using Raman microscopy on different parts of the ball wear scar (**Figure 10a**), the presence of MoS_2 could be confirmed. In contrast to steel/steel systems, huge black deposits are found next to the edge of the ball wear scar. These deposits were found to consist of a mixture or composite material made of carbonaceous species and MoS_2 (**Figure 10a**). These carbonaceous deposits result from the degradation of the DLC coating, as they were not detected in the steel/steel contact. As for the disk, shown in **Figure 10b**, the MoS_2/Carbon peaks were detected in the deposits at the edge of the wear scar. The strong D, G signals found in these deposits are attributed to the a-C:H coating underneath the deposit.

The most interesting fact is that no sign of MoS_2 is found on the wear scar (not even a weak signal as detected in the steel/steel case). No MoO_3 or other molybdenum hard oxides were detected, and the wear scar showed less roughness than the original surface (R_a=0.04 µ), pointing towards the sequestration of C-H bonding as the most likely mechanism leading to coating destruction, in agreement with most recent papers [35, 50].

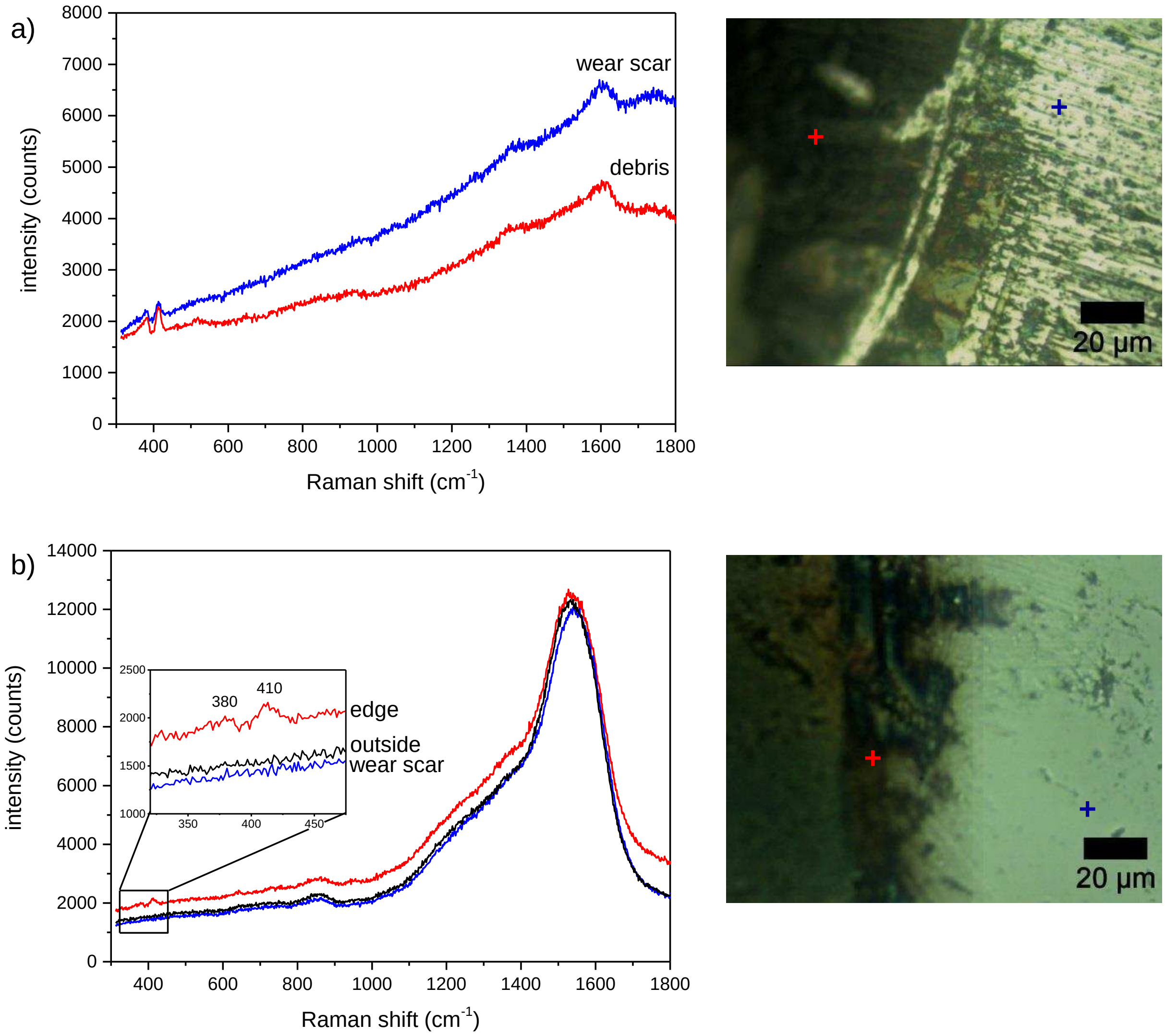


Figure 10. Raman analysis of a) steel ball, and b) a-C:H disk, in a BO+MoDTC lubricated test.

The performance of BO+MoDTC lubricant in ta-C is characterised by the extremely low coefficient of friction and no measurable wear to the coating. Analyzing the ta-C coated disk, MoS_2 was detected all over the tribolayer (**Figure 11a and b**), explaining the low friction measured in this test. In contrast to a-C:H case, ta-C shows a MoS_2 rich tribolayer in the center of the wear scar.

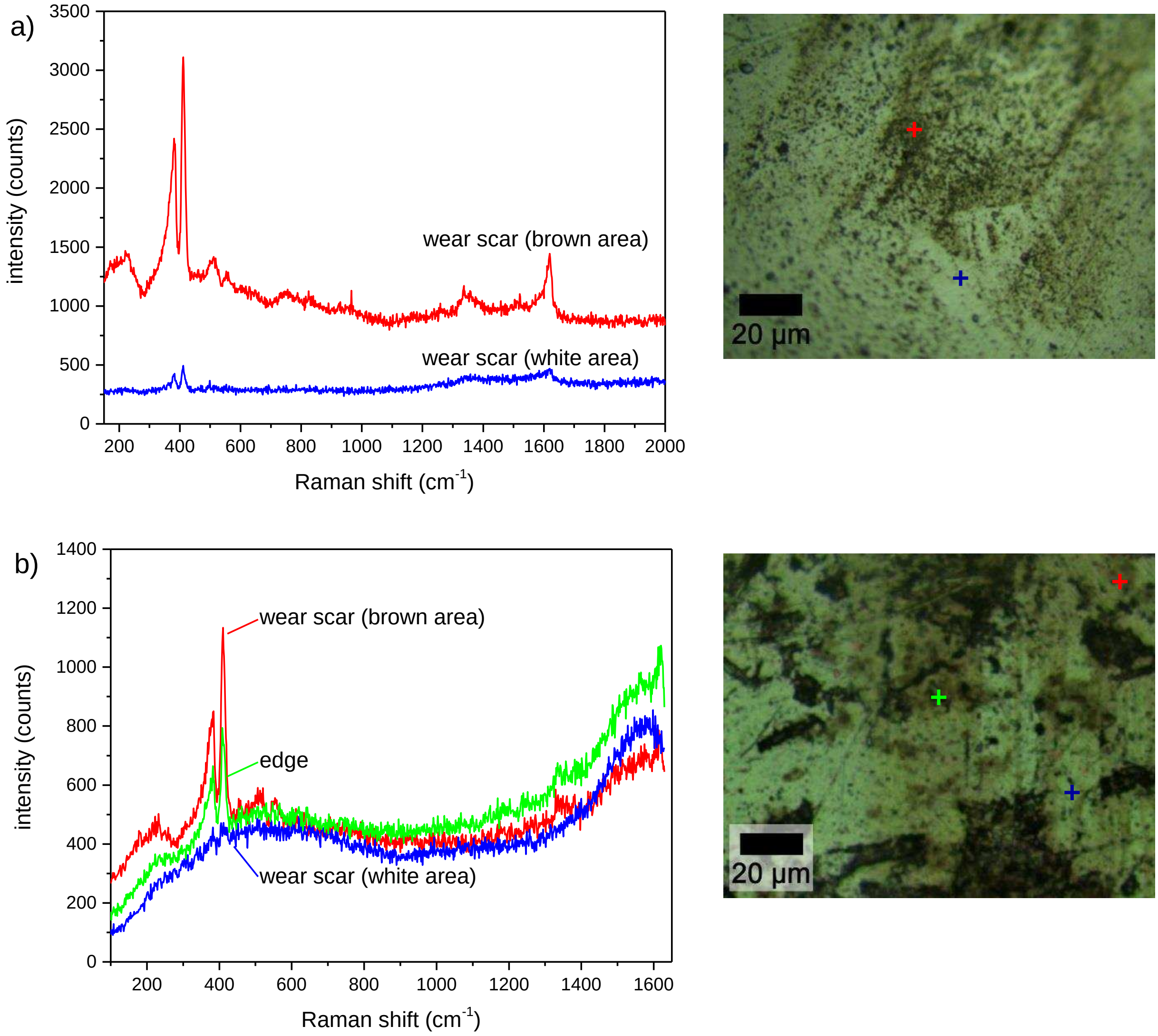


Figure 11. Raman analysis of a) steel ball, and b) ta-C coated disk, in a BO+MoDTC lubricated test.

Based on the results obtained in this work, it is evident that the hydrogen content plays a crucial role in the tribolayer formation and tribological performance when MoDTC is used as an additive. As indicated earlier, differences in wear behavior between hydrogenated and non-hydrogenated DLCs are reported in the literature [51]. However, no clear relationship has been established between the presence of molybdenum oxides or sulfides detected with XPS and the coating accelerated wear. Using Raman microscopy, clear MoS_2 formation differences in these two coatings have been determined: The a-C:H accelerated wear found in this work was accompanied by a lack of MoS_2 on the DLC wear track, being MoS_2 only present in the ferrous counterpart (similarly to de Feo et al. [35, 49]); whereas ta-C coating, not only did not show accelerated wear, but also a unequivocal MoS_2-containing tribolayer patchily distributed on the contact area in both the ta-C disk and the steel ball counterpart.

3.3.3. Fully-formulated oil lubricated tests

When FF lubricant was used, both the tribological behavior and the tribochemistry change with respect to model lubricants. To begin with, FF lubricant generates an antiwear Raman-fluorescent tribolayer on steel/steel contact **(Figure 12a)**. Fluorescence is common in tribolayers obtained from fully formulated oils containing antiwear additives [60, 61], rendering a huge background and difficult results interpretation. The nature of the tribolayer is patchy, with Raman sensitive and non-Raman sensitive areas. Fe_3O_4 and fluorescence is detected, but not other oxides as Fe_2O_3 which are detected in base oil lubricated contacts are found. This suggests the antiwear tribolayer passivates the ferrous surface, inhibiting oxidation under rubbing contact.

In steel/a-C:H contact, shown in **Figure 12b**, the steel ball wear scar shows similar Raman spectra, evidencing the formation of a tribolayer that blocks the formation of hematite on the steel surface.

Steel/ta-C system lubricated with the FF lubricant produces a Raman fluorescent tribolayer on the steel ball wear scar (see **Figure 12c**). In this case, the level of fluorescence is much lower than that of both steel/steel and steel/a-C:H contacts, indicating very thin or no tribolayer formed on the wear scar. The lack of tribolayer on the steel/ta-C contact explains no wear reduction of the steel ball when the FF lubricant was used. Coatings have different reactivity towards lubricant additives and ZDDP formation. As a result, an effective anti-wear tribolayer may be or may be not formed, depending on every particular coating/lubricant system [18, 62].

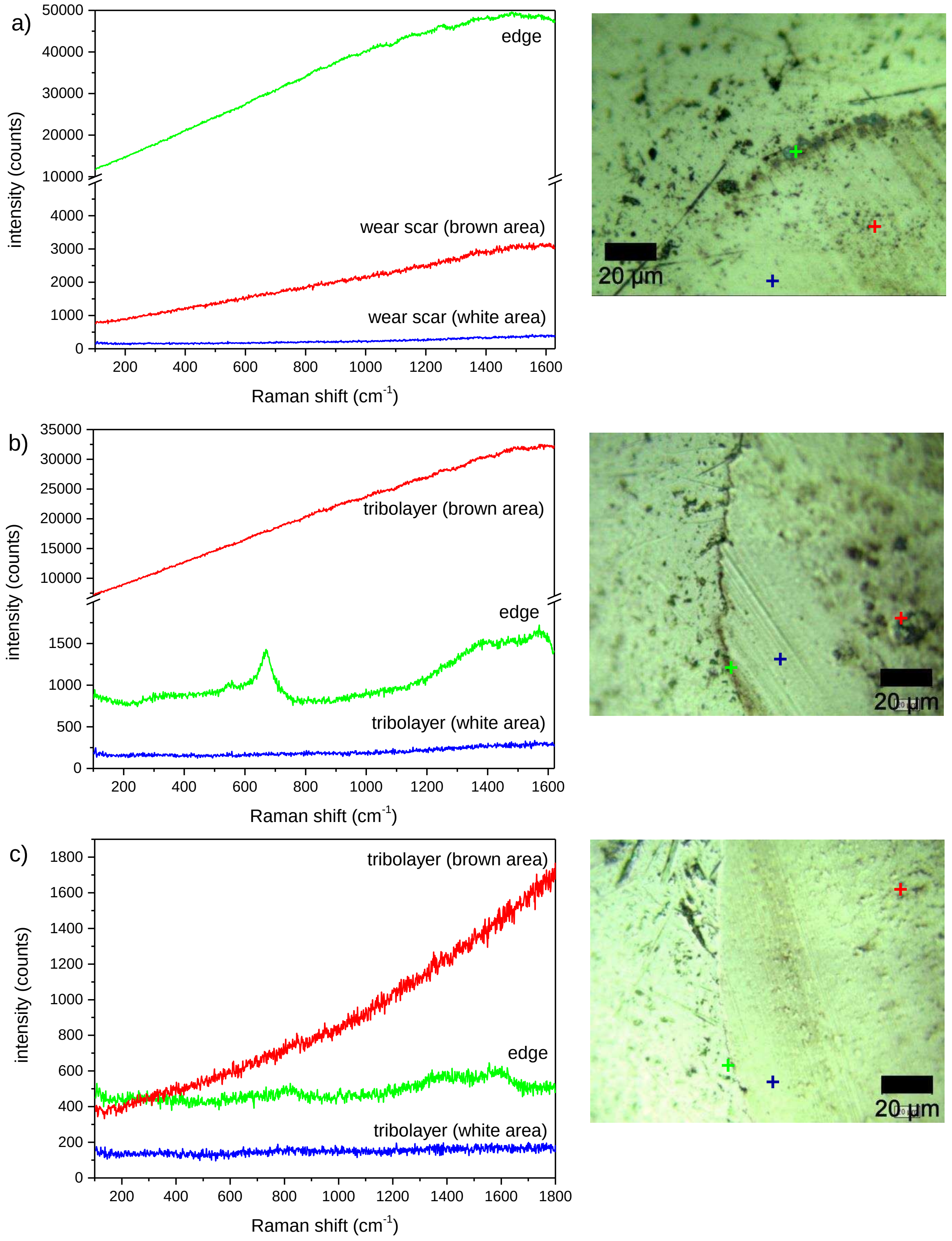


Figure 12. Raman microscopy on different steel balls tested using FF as a lubricant: a) steel/steel, b) steel/a-C:H, c) steel/ta-C.

3.3.4. Fully-formulated oil with MoDTC lubricated tests

When lubricating a steel/steel system with a FF+MoDTC lubricant, the wear of both disk and ball components was lower compared to wear obtained from BO+MoDTC lubricated tests. This is not surprising, as the FF lubricant contains other additives which are known to form protecting tribolayers on steel surfaces. **Figure 13a** shows Raman spectra on several points of the wear scar. The tribolayer, brownish in color, is shown to fluorescent, similarly to FF tested samples. No MoS_2 Raman peaks were detected, explaining the lack of friction reduction with this lubricant. Despite the positive effect of antiwear additives on MoS_2 formation, the presence of other additives (dispersants, antioxidants, etc.) could hinder MoS_2 formation [23, 42]. Further work is required to confirm this.

Friction and wear performance of the coated systems depended on the type of coating used. In both cases, no wear scar or tribolayer was found on the disks. Hence, the Raman analysis was performed only on steel ball wear scar. **Figure 13b** shows several spectra of the steel ball after a-C:H tests. In this case, MoS_2 is found all over the tribolayer. These results indicate that both the type of the coating and the lubricant additives used with the MoDTC play a crucial role in MoS_2 formation on the steel counterface, while preventing the excessive coating wear observed when BO+MoDTC lubricant was used. However, the presence of MoS_2 on the steel ball wear scar did not result into further friction reduction, with respect to the already low friction behavior achieved with the a-C:H/system in a BO lubricated contact. In this system, the effect of the surface chemistry prevails over the MoS_2 friction-reducing capabilities.

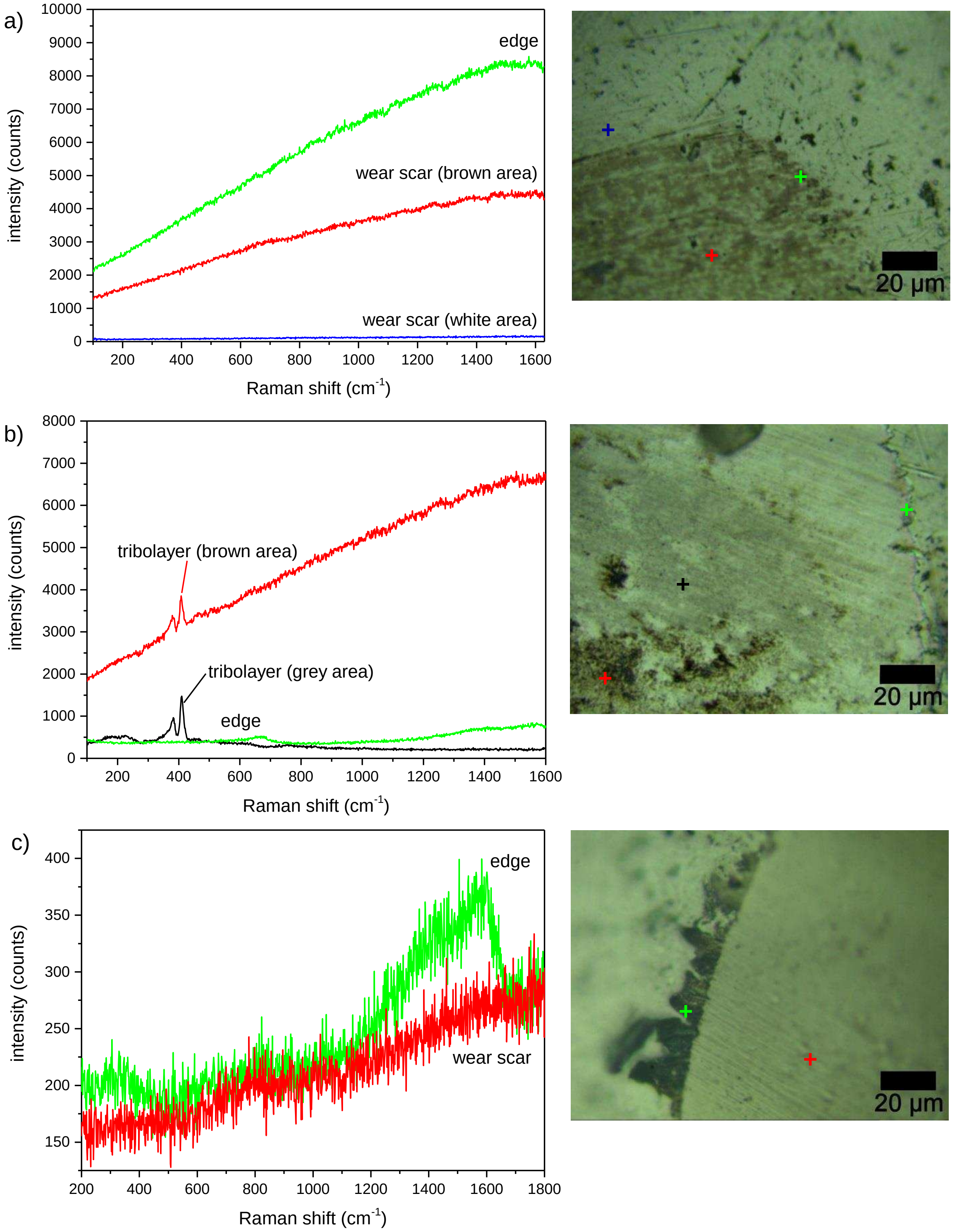


Figure 13. Raman microscopy on different steel balls tested using FF+MoDTC as a lubricant: a) steel/steel, b) steel/a-C:H, c) steel/ta-C.

As for the steel/ta-C system, no Raman active tribolayer was detected on the ta-C coating nor the steel counterface (**Figure 13c**). Carbonaceous material is observed on the edges of the steel ball. This material could come from the oil, as no visible damage or interaction is produced on the ta-C coating counterpart. No positive low-friction tribolayer is formed, due to interactions with other additives, especially detergents, dispersants and antioxidants [42].

3.3.5. Summary

Table 5 summarizes main tribolayer characteristic features observed for both disk and ball for every lubricant/surface combination. This table highlights the differences in tribolayer formation depending on the coating and lubricant used.

Table 5. Tribolayer features for every pair/lubricant used in this study.

Lubricant / Material	BO	BO+MoDTC	FF	FF+MoDTC
Steel ball / steel disk (ball)	Iron oxides rich tribolayer.	MoS_2 patchy tribolayer. MoS_2/carbon material debris.	Anti-wear tribolayer.	Anti-wear tribolayer.
Steel ball / steel disk (disk)	Iron oxides rich tribolayer.	MoS_2 containing layer. Larger amount in the edges of the wear scar. MoS_2/carbon material debris.	Anti-wear tribolayer.	Anti-wear tribolayer.
Steel ball / a-C:H disk (ball)	Carbon transfer layer, no oxides.	MoS_2 patchy tribolayer. Huge MoS_2/carbon debris.	Anti-wear tribolayer. Some carbon transfer layer.	MoS_2 patchy tribolayer.
Steel ball / a-C:H disk (disk)	No measurable wear. Slight abrasion lines.	MoS_2 at the edge of the wear scar. High polishing wear.	No tribolayer or wear scar.	No tribolayer or wear scar.
Steel ball / ta-C disk (ball)	Iron oxides rich tribolayer. Some carbonaceous material at the edges.	MoS_2 patchy tribolayer. No carbon transfer layer.	Anti-wear tribolayer.	Anti-wear tribolayer. Some carbonaceous material at the edge.
Steel ball / ta-C disk (disk)	No tribolayer or wear scar.	MoS_2-containing patchy tribolayer.	No tribolayer or wear scar.	No tribolayer or wear scar.

MoDTC reactivity on steel/steel tribological systems, assessed by the detection of MoS_2 in the tribolayer, is directly related to the friction performance. The presence of the full additive package in the oil leads to negative interactions with the MoDTC additive which prevents MoS_2 formation [63]. Although the recommended amount of additive is 500 ppm of molybdenum for base oils blends [6], higher concentration would be needed to obtain a molybdenum containing friction reducing tribolayer [45] and achieve fuel economy [64], especially for a steel/DLC system.

The most noticeable differences between a-C:H and ta-C occur however in MoDTC presence. In agreement with literature [49, 51], hydrogen-containing DLC in combination with MoDTC and a steel counterface produces an accelerated wear of the coating and a huge production of MoS_2 and graphite-like carbonaceous material. This effect is not produced in the ta-C coating system, where a stable MoS_2 containing tribolayer is formed on the DLC disk instead without any measurable wear loss. According to the MoS_2 mechanism from MoDTC [25], MoS_2 would be formed either on the steel part or ferrous based debris, and then transferred into the DLC coating. In the case of a-C:H coating, the formation of MoS_2 was seen to be accompanied by the formation of the carbonaceous layer, as detected with Raman analysis in this study and with other techniques in other works [32, 65]. This was not the case with the ta-C coating. In this coating, the MoS_2 was the main chemical species detected on both steel and ta-C wear scar when lubricated with BO+MoDTC oil. These results indicate that the a-C:H wear with MoDTC is related to the formation of the carbonaceous layer on the wear scar.

Presence of the other additives in the lubricant (FF+MoDTC lubricant) eliminated the excessive a-C:H coating wear, while still forming a MoS_2 tribolayer on the surface.

The behavior of MoDTC in the steel/ta-C system is similar to the one in steel/steel system in terms of tribochemistry and tribological performance. While the friction and wear performance of the steel/ta-C system is defined by mainly the reactivity of steel towards MoDTC and other additives in the FF lubricant, in steel/a-C:H systems the additives seems to be reactive to both steel and the a-C:H coating resulting in unexpected high coating wear.

4. Conclusions

In this study, the performance of MoDTC-containing model and fully formulated lubricants was tested in three materials combinations. This performance was then correlated to the tribolayers formed on the wear scar. The key conclusions are:

1. Steel/DLC systems exhibit less friction and more wear in the steel counterface for every lubricant in comparison to steel/steel systems used due to the surface chemistry and the hardness differences between steel and DLC.
2. The a-C:H coating lubricated with BO+MoDTC results in high coating wear. In this system, the presence of molybdenum additive results in not only MoS_2 formation, but also in formation of large carbonaceous deposits on the steel counterface. Formation of the carbonaceous layer is related to high wear and is a result of the chemical reaction between MoDTC and a-C:H coating.
3. A positive effect is produced with BO+MoDTC in ta-C systems yielding a very low friction coefficient and little to no wear in the coating. For the first time, a distinctive MoS_2-containing tribolayer is detected on a DLC coating, leading towards a very low friction coefficient (below 0.04).
4. When MoDTC is blended in a fully formulated oil, no friction reducing-MoS_2-containing tribolayer is formed because of negative interactions with other additives contained in the fully formulated oil. Presence of these additives prevented the excessive a-C:H coating wear even when the MoDTC was present in the lubricant.

This work showed for the first time that the MoS_2 tribolayer can be formed on a ta-C coating and the mechanism by which this is achieved are discussed. It has also shown that coating reactivity towards the MoDTC leads to high coating wear, and that the other lubricant additive can affect this tribochemical reaction. Further research is underway to obtain the optimum balance between additive/additive and additive/a-C:H chemical interactions for achieving low friction and durable coating.

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