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Kosarieh, S, Morina, A, Laine, E et al. (2 more authors) (2013) The effect of MoDTC-type friction modifier on the wear performance of a hydrogenated DLC coating. Wear, 302 (1-2). 890 - 898. ISSN 0043-1648

https://doi.org/10.1016/j.wear.2012.12.052

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The effect of MoDTC-type friction modifier on the wear performance of a hydrogenated DLC coating

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Abstract:

The application of Diamond-Like Carbon (DLC) coatings for automotive components is becoming a promising strategy to cope with the new challenges faced by automotive industries. DLC coatings simultaneously provide low friction and excellent wear resistance which could potentially improve fuel economy and durability of the engine components in contact. The mechanisms by which a non-ferrous material interacts with a variety of lubricant additives is becoming better understood as the research effort in this area increases however there are still significant gaps in the understanding . A better understanding of DLC wear may lead to lubricant additive solutions being tailored for DLC surfaces to provide excellent durability (wear) as well as similar or increased fuel economy (low friction). In this work, the wear and friction properties of DLC coating under boundary lubrication conditions have been investigated.

A pin-on-plate tribotester was used to run the experiments using HSS steel plates coated with 15 at.% hydrogenated DLC (a-C:15H) sliding against cast iron pins. One type of fully formulated oil with and without ZDDP and two levels of a MoDTC type friction modifier (Mo-FM) was used in this study. The friction and wear response of the fully formulated oils is discussed in detail. Furthermore, optical and scanning electron microscopes (SEM) were used to observe the wear scar and obtain wear mechanisms. Energy-Dispersive X-ray analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS) analysis were performed on the tribofilms to understand the tribochemical interactions between oil additives and the DLC coating. A nano-indentation study was conducted to observe the changes in the structure of the coating, which can

provide a better insight into the wear mode and failure mechanism of such hard coatings.

In the light of the physical observations and tribochemical analysis of the wear scar, the wear behaviour of a hydrogenated DLC (a-C:15H) coating was found to depend on the concentration of the MoDTC friction modifier and the wear performance is much better when ZDDP is present in the oil. The tribochemical mechanisms, which contribute to this behaviour, are discussed in this paper.

1 Introduction

Diamond-Like Carbon (DLC) coatings have become an attractive surface engineering solution in the automotive industry as they offer excellent tribological performance including low coefficient of friction, high wear resistance [1, 2] and outstanding running-in properties [2]. Diamond like carbon coatings have similar properties to diamond but are amorphous carbon coating consisting network of sp^2 (graphite-like), sp^3 (diamond-like) and hydrogen bonds.

Commonly used lubricant additives are designed to form tribofilms on ferrous-base surfaces. It is therefore essential to optimise coating and lubricant compatibility to enable additive solutions to be tailored to DLC surfaces. The properties of DLC coatings depend extensively on the sp^2/sp^3 ratio as well as hydrogen content, which in return, depends on the deposition process and applied parameters [3]. Thus, the interaction between lubricant additives and DLC depends significantly on the type of DLC used.

Molybdenum Dithiocarbamates (MoDTC) and Zinc Dialkyldithiophosphates (ZDDP) are well-known friction modifier and antiwear additives respectively, used for ferrous surfaces. Having low shear strength, MoS_2 low friction crystals, derived from MoDTC decomposition, provide low friction at the tribological contacts in boundary lubrication conditions [4-6]. ZDDP offers antiwear properties by forming sulphide- and phosphate-containing tribofilms at ferrous surfaces [5-7]. It has also been suggested that the presence of

ZDDP could promote MoS_2 formation and that ZDDP may enhance durability of the MoS_2 sheets [8, 9]. In addition, MoDTC has been found to improve the wear resistance of the ferrous surfaces by forming N-containing species in the tribofilm [5].

Different researchers have started to evaluate interactions between lubricant additives with various types of non-ferrous DLC coatings under boundary lubrication. DLC coatings have been reported to be chemically inert using a steel pin sliding against DLC-coated disks lubricated in oil containing MoDTC and/or ZDDP [10]. In contrast, molybdenum-based friction modifiers and ZDDP antiwear have been reported to form low friction MoS_2 sheets and/or ZDDP-derived compounds respectively, on the DLC coating providing low friction and better wear performance under boundary lubrication conditions [11-17].

Recently, the effect of MoDTC in increasing wear of a DLC coating in a DLC/steel contact has been reported [16, 18-23]. Haque et al. [16] showed that DLCs rubbed against steel in the presence of a MoDTC-containing base oil gave extremely high wear but that the addition of the antiwear additive ZDDP terminated this effect [16]. Sugimoto [20] also reported the higher wear of DLC in a DLC/steel system when lubricated in MoDTC-containing fully formulated oil. In contrast, Tung et al. [24] showed that MoDTC can reduce the wear of a DLC coating lubricated in fully formulated engine oil which could be due to the fact that ZDDP was present in his oil and could suppress the effect of MoDTC on promoting wear of DLC coatings reported by others. Recent literature on the harmful effect of Mo-containing friction modifier in promoting high wear of DLC is summarised in Table 1.

The origin of “MoDTC induced wear” on DLC is not fully understood and previous studies mainly used single additive solutions rather than realistic fully formulated oils. Furthermore, the addition of ZDDP to the lubricant has been shown to cancel or reduce the effect of MoDTC in promoting wear on DLC coatings, but it has not been reported whether other surface active additives in the oil could provide similar protection. Therefore, a comprehensive understanding of the DLC/MoDTC interaction is still to be clearly produced. The main objective of this work is to study the effect of a MoDTC-type friction modifier (Mo-FM) concentration on the wear performance of 15 at.% hydrogenated DLC coating (a-C:15H) under boundary lubrication conditions using fully formulated oils.

Table 1 Summary of literature on the effect of MoDTC in promoting high wear of DLC coatings.

Author(s)	System	Type of DLC	High wear for DLC coating observed with:			Wear Mechanism
			Model oils		Fully formulated oils	
			MoDTC	ZDDP +MODTC		
Tung et al.,[24]	DLC/CI	Not mentioned	-	-	No	A protective tribofilm produced by MoDTC with ZDDP, which acts to reduce wear.
Shinyoshi et al.[19]	DLC/steel	Not mentioned	Yes	-	-	Oxidative wear due to reaction of MoO_3 with the DLC active sites.
Haque et al.[16, 18]	DLC/CI	a-C a-C:15H	Yes (Multiple sources)	No	-	In the absence of ZDDP, high pressure exerted by small third body particles could go beyond the endurance limit of the coating.
Vengudusamy, B., et al.[21]	DLC/steel	a-C a-C:H Si-DLC	Yes	-	-	“Pro-wear process must involve the presence of the steel counterface”
	DLC/DLC		No	-	-	
Sugimoto [20]	DLC/steel	a-C:H	-	-	Yes	Graphitization of the DLC followed by the formation of hard Mo compounds on the steel counterpace accelerating the wear on the DLC plate.

2 Experimental details

2.1 Pin-on-plate tests

Tests were conducted using a reciprocating pin-on-plate tribometer under boundary lubrication conditions. The samples were cleaned prior to the start of the test using acetone. The tests temperature was set at 100°C and the contact point of the plate and the pin was lubricated under a static volume of oil (3 ml). The average linear speed was 20 mm/s (stroke frequency of 1 Hz). A load of 390N was applied providing an initial Hertzian contact pressure of 0.7 GPa resembling a pressure range to a Lowcam/follower contact gasoline engine. The duration of the tests was 20 hours and the friction force data was recorded every minute corresponding to two cycles. For a more precise evaluation of the friction performance, each type of test was repeated at least three times and the average repeatability was found to be less than 0.007 for the friction coefficient in the steady state region (i.e. last hour of the tests).

2.2 Materials

Tests were carried out in the pin-on-plate tribotester using cast iron (CI) pins and coated HSS M2 Grade steel plate. The dimensions of the CI pin were 20 mm in length, diameter 6 mm and the ends of the pins had a 40 mm radius of curvature. The geometry of the plate was 15 mm×6 mm× 3mm. The physical properties of the substrate, coatings and pin are given in Table 2.

Table 2. Physical properties of plates (substrate/coatings) and counterpart materials

Properties of coating and other related materials	Ferrous Material		DLC Coating
Specification	HSS M2 Grade	Cast iron BS1452	a-C:15H [a]
Hardness	8.0 GPa	4.0 – 4.5 GPa	17.0 GPa
Reduced Young's modulus	218 GPa	134 GPa	190 GPa
Roughness, R_q	0.04-0.06 µm	0.07-0.09 µm	0.04-0.06 µm
Composition/ Coating thickness	C 0.64%, Si 0.55%, Cr 1.57%, and Mn 0.49%	C 3.0%, Si 2.0%, Mn 0.4%, Cr 0.1%, Cu 0.3%	≈3 µm CrN Intermediate layer <0.5 Cr adhesion layer 2-3 µm coating

[a] Commercial coatings obtained from Oerlikon Balzers Ltd., UK.

A hybrid unbalanced magnetron sputter ion plating/PECVD deposition system was used to deposit the a-C:15H coating on the steel plate. First the substrates were cleaned by Ar^+ plasma ion etching using pulsed DC bias followed by deposition of a thin adhesion promoting Cr layer by DC magnetron sputtering with a pulsed DC bias. A CrN intermediate layer was then deposited by introducing nitrogen gas into the chamber. Finally, by adding a hydrocarbon gas, a layer of the a-C:15H coating was deposited using a plasma enhanced chemical vapour deposition (PECVD) technique, where a pulsed DC bias was applied on the substrate and a discharge enhancing electrode with a 13.56-MHz RF generator was used.

2.3 Lubricants

The lubricants used in this study are one type of fully formulated oil with and without ZDDP and two levels of a MoDTC type friction modifier (Mo-FM). In addition, organic friction modifier (OFM), detergent, dispersant and antioxidant are present in all of the lubricants. All the oils are supplied by Infineum UK limited and considering that they are commercial lubricants, some chemical details are not possible to release. However, the key additive components in each oil are shown in Table 3.

Table 3. Lubricant components

Lubricants	Annotations	ZDDP	Mo (ppm)	P (ppm)*
Fully formulated oils	Low+	+	40	750
	Low-	-	40	-
	High+	+	300	750
	High-	-	300	-

*All FF oils contain organic friction modifier (OFM), detergent, dispersant and antioxidant.

Considering load, material and lubricant properties, the film thickness and lambda ratio were calculated using equations Eq 1 and Eq 2 respectively. h_{min}, minimum film thickness, is numerically defined as [25, 26]:

$$\frac{h_{min}}{R'} = 3.63\left(\frac{U\eta_0}{E'R'}\right)^{0.68}\left(\alpha E'\right)^{0.49}\left(\frac{W}{E'R'^2}\right)^{-0.073}\left(1-e^{-0.68k}\right) \quad \text{Eq 1}$$

Where η_0 is the dynamic viscosity at atmospheric pressure of the lubricant (4.03×10^{-3} Pas), α is the viscosity-pressure coefficient (1.1×10^{-8} Pa^{-1}), R' is the reduced radius of curvature (20 mm), U is the entraining surface velocity (20 mm/s), W is the normal load (390 N), E' is the the reduced Young's modulus. The dynamic viscosity and viscosity-pressure coefficient were measured at 100°C.

$$\lambda = \frac{h_{min}}{\sqrt{R_{q_1}{}^2 + R_{q_2}{}^2}} \quad \text{Eq2}$$

Where R_{q_1} is the roughness of the coating and R_{q_2} is the roughness of the pin end.

The calculation gives the lambda ratio well under the unity (0.002) implying that the lubrication is in boundary regime.

2.4 Surface analysis

2.4.1 Wear Measurements

The plate wear was measured using a Veeco WYKO (optical white light interferometer). The pin wear are calculated from the wear diameter on the counterbody (pin) to indicate the lubricant effectiveness in wear reduction in the overall lubricating system. The wear scar diameters on the pins are calculated using the optical microscope and then the volume of the lost segment of the sphere is calculated. Finally, the specific wear coefficients have been calculated using the Archard wear equation.

$$\boldsymbol{K_i} = \frac{\boldsymbol{V_i}}{\boldsymbol{F} \times \boldsymbol{S}} \quad \text{Eq3}$$

Where F is the normal load (N), S the sliding distance (m), V_i the wear volume (m^3), K_i and the dimensional wear coefficient and index i identifies the surface considered.

2.4.2 Coating wear analysis

In this study, a Zeiss EVO MA15 Variable Pressure SEM was used to investigate the mechanism of wear and the durability of the coatings. It was integrated with an Oxford Instruments Energy Dispersive X-ray (EDX) analysis system. In this study, the EDX analysis was used to provide information about the durability of the coating. EDX mapping obtained within the wear tracks showed the presence of C and Cr. Cr comes from the underlying CrN/Cr intermediate layer and so could be used as a qualitative analysis of the extent of the coating wear. The higher the Cr intensity in the EDX maps, the higher removal of coating thickness due to wear (Figure 1).

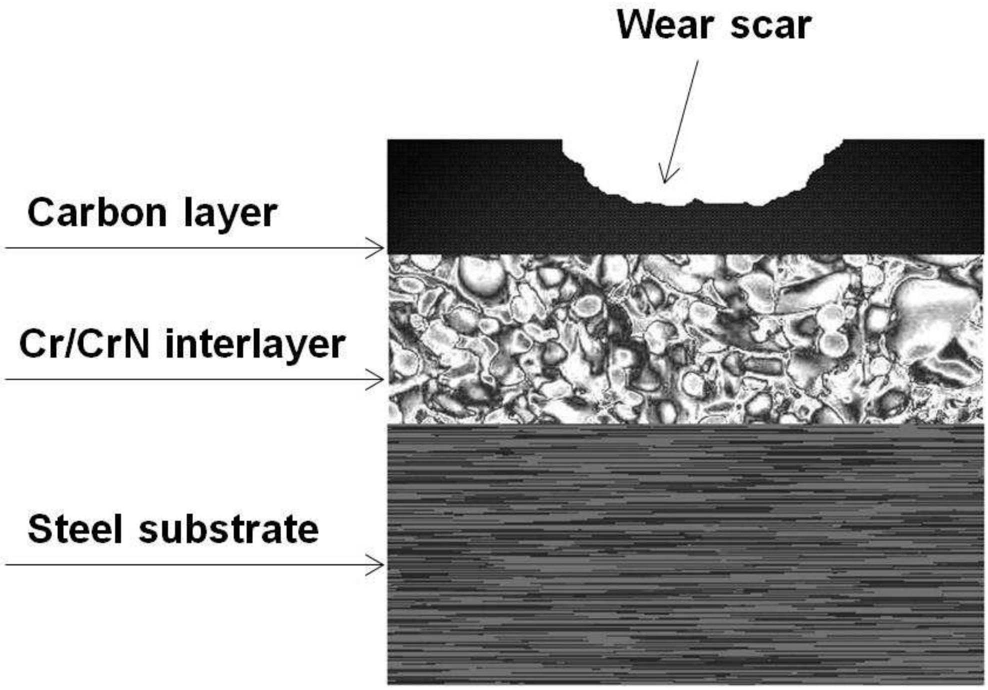

Figure 1 Schematic diagram showing the cross section of the a-C:15H coating plate. Concentration of Cr, detected by EDX, is higher inside the wear track compared to outside.

2.4.3 Nano-indentation analysis

Mechanical properties of the coatings are obtained by nano-scale indentation using a Micro Materials Limited NanoTest™ Platform One device. The indentations are performed in a controlled environment temperature of 25 ^{o}C, using a Berkovich-type indenter. As a result of the measurement, the force–displacement curve is produced. By analysing the recorded results, the mechanical properties such as hardness and modulus of elasticity are obtained.

The indentation load was set at 5 mN, resulting in a maximum indentation depth of 100nm in the coating. A thermal drift setting of 60 s was used so that the material could settle within temperature variations caused by the indentation process. A standard indentation grid of four rows by three columns was chosen arbitrarily and was applied to all samples. The indenter is tested for accuracy every week using a standard silicon plate that has known hardness values.

2.4.4 Chemical analysis of the tribofilms

XPS analysis measurements were made on the tribofilm formed on the plate surfaces. This surface sensitive technique can analyse very top layer of the surface (5 nm depth). Any residual oil and/or contaminants were removed by soaking the samples in N-heptane for 10 seconds prior to the XPS analysis. An area of 500 µm× 500 µm in the wear scar of the plates has been analysed using a monochromatized Al K[α] source in the XPS. Spatial mode was chosen to acquire all the spectra. The curves on the XPS peaks obtained from long scans were fitted using CasaXPS software [27] and the quantitative analyses of the peaks were performed using peak area sensitivity factors. The chemical species corresponding to each binding energy have been found using a handbook of XPS [28]. The position of C1s peak (284.8 eV) was considered as the reference for charge correction. The peak area ratio, difference between binding energies of the doublets, and full-width at half-maximum (FWHM) were constrained to provide the most appropriate chemical meaning. A linear background approximation was used to process the data in this study.

3 Results

3.1 Friction Results

The friction coefficient as a function of time for the a-C:15H/CI combination using four different oils is given in Figure 2 . Based on the friction traces, it can be seen that a drop in friction was observed only with fully formulated oils with high concentration of Mo-FM. The average friction coefficients of the last hour of the tests as a function of Mo-FM concentration for a-C:15H/CI system are presented in Figure 3. Overall, friction was observed to be oil dependent and reduced with an increase in Mo-FM concentration as expected. Based on the friction results, it can be seen that Mo-FM was not effective in friction reduction with Low concentration while increasing the Mo-FM level in the oils resulted in lower values for friction. The presence of ZDDP in the formulated oils with the high level of Mo-FM gave rise to an increase in friction in comparison to the non-ZDDP containing oils (High-) as has been widely reported.

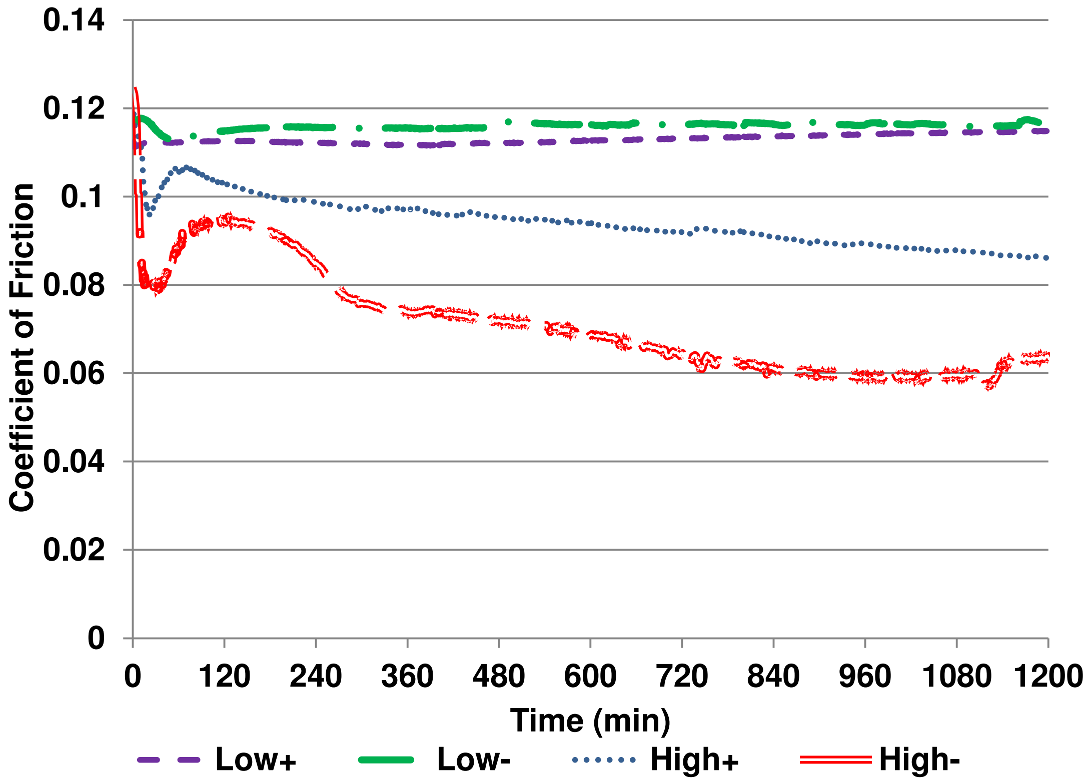

Figure 2 Friction traces as a function of time for the a-C:15H/CI system for Low+, Low-, High+ and High-.

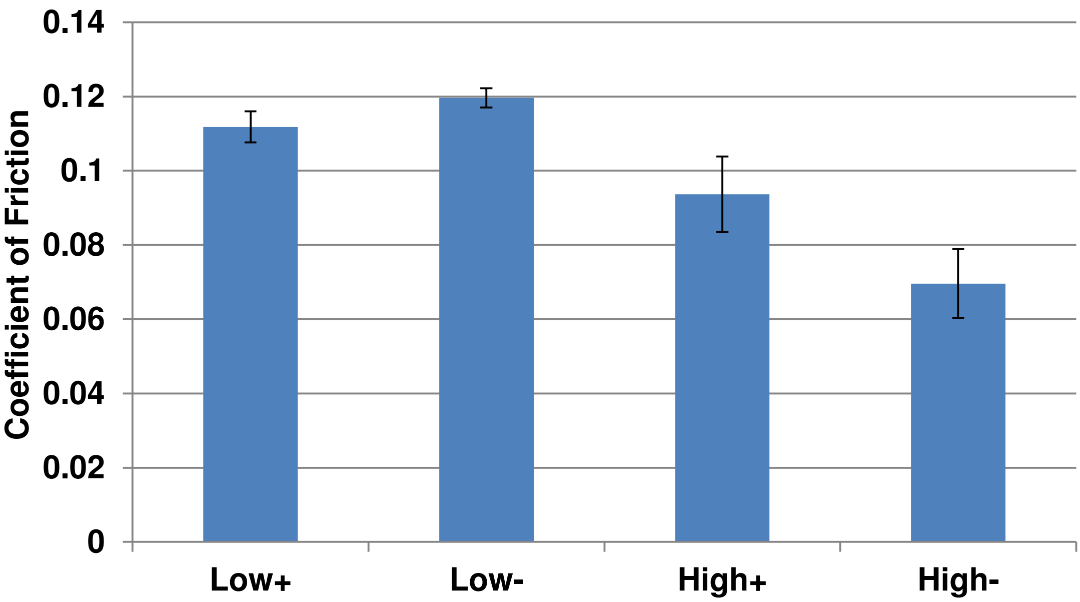

Figure 3. Steady state friction coefficients as a function of Mo-FM concentration for a-C:15H/CI system.

3.2 Coating durability and wear results

The wear coefficients of different a-C:15h coated plates as a function of Mo-FM concentration calculated using Eq3 for a-C:15H coating are given in Figure 4. It is evident that the higher the Mo-FM, the higher the wear. The wear provided by lowest Mo-FM concentration containing fully formulated oils (Low+ and Low-) on a-C:15H/CI system were observed to be extremely low while increasing Mo-FM concentration significantly increased the wear. However, it is interesting to note that the addition of ZDDP significantly improved the wear performance; this is clear by comparing High+ with High-.

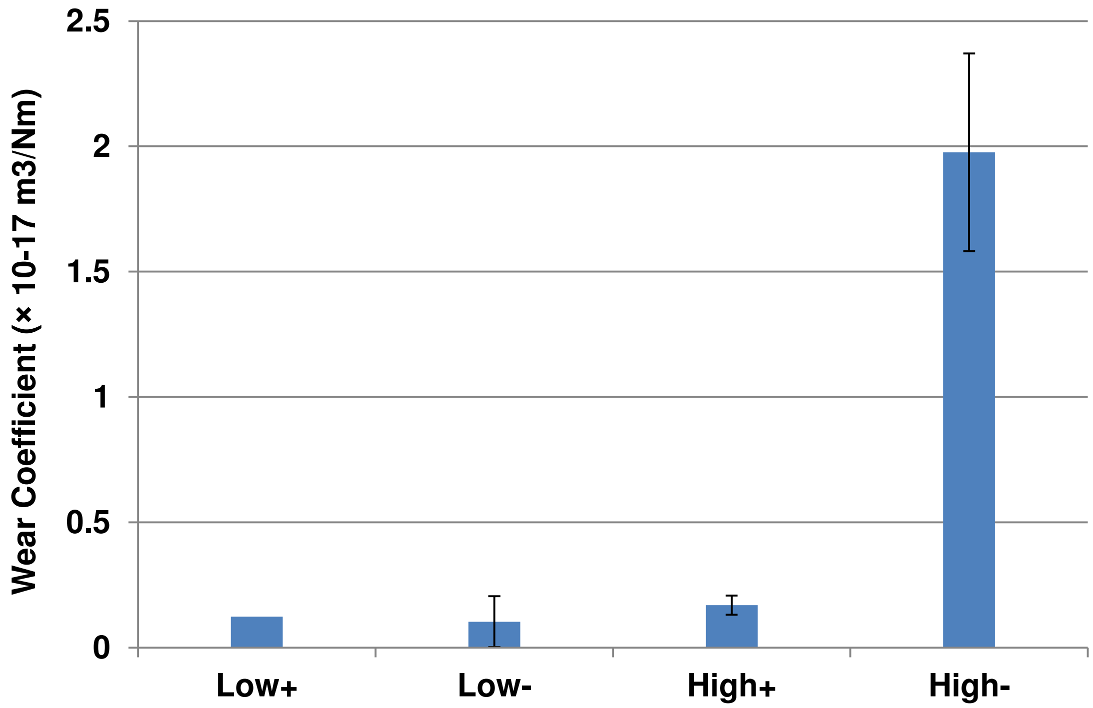

Figure 4 Wear coefficient as a function of Mo-FM concentration for a-C:15H/CI system.

Figure 5 shows representative images of the wear scar; it is evident that the extent and mechanisms of wear are dependent on the additive package used in the lubricant. Based on the optical images, the colour of the wear tracks were brighter than outside of the wear tracks suggesting the relation of underlying Cr/CrN layers, as a result of the loss of coatings.

Delamination of the coatings was not observed using any of the oils (Figure 5a-d); rather, the wear of the coatings was dominated by gradual polishing wear. It should be mentioned that, in this study, the term “delamination” refers to the adhesion failure or removal of coating from the substrate. Additionally, the average depth of the wear tracks of a-C:15H coating for the highest obtained wear, provided by High- oil, was approximately 0.72 µm over the duration of the test when compared to the best wear performance by Low- oil which was only 0.03 μm.

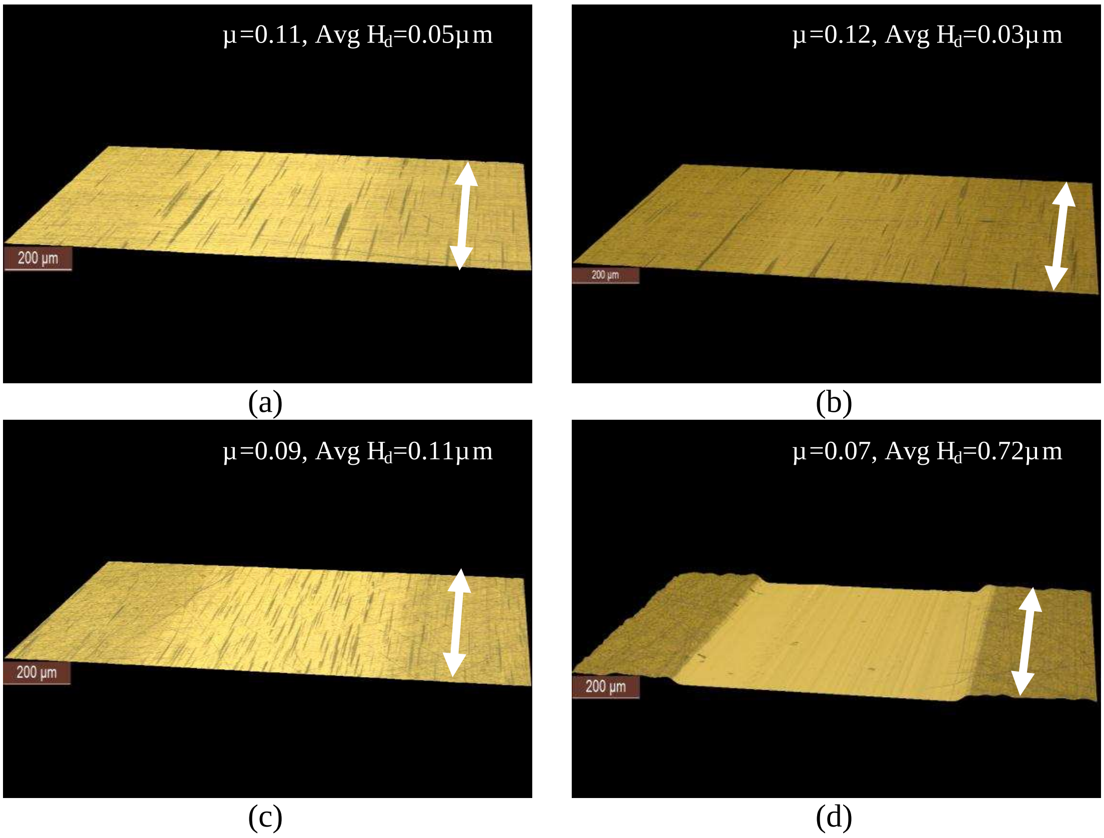

Figure 5 Optical images of the wear scars formed on the a-C:15H coated plates using (a) Low+, (b) Low-, (c) High+, (d) High-. The arrows on the images show sliding directions.

To verify the observations from wear results and optical microscope images, EDX was carried out in the wear scar. The EDX measured the level of Cr from the Cr interlayer as a measure of coating thickness loss. The plates were cleaned by acetone in ultrasonic bath to remove any residual oil and physisorbed films prior to the SEM/EDX analysis. It is important to note that, the SEM/EDX analysis in this study was performed to check the durability of coating, not to characterize tribofilms.

Shown in Figure 6 is the representative secondary electron (SE) image of a section of a-C:15H coating wear scar along with EDX mapping of C, Cr and Fe after the pin-on-plate tests. It is obvious that EDX mapping of a sample with higher wear provides lower carbon, higher chromium and some iron (in some cases) in the wear scar. Based on the mapping images, fully formulated oils with low level of Mo-FM showed very little difference in concentration of C and Cr comparing inside and outside of the wear scar implying extremely low gradual wear on the coated plates.

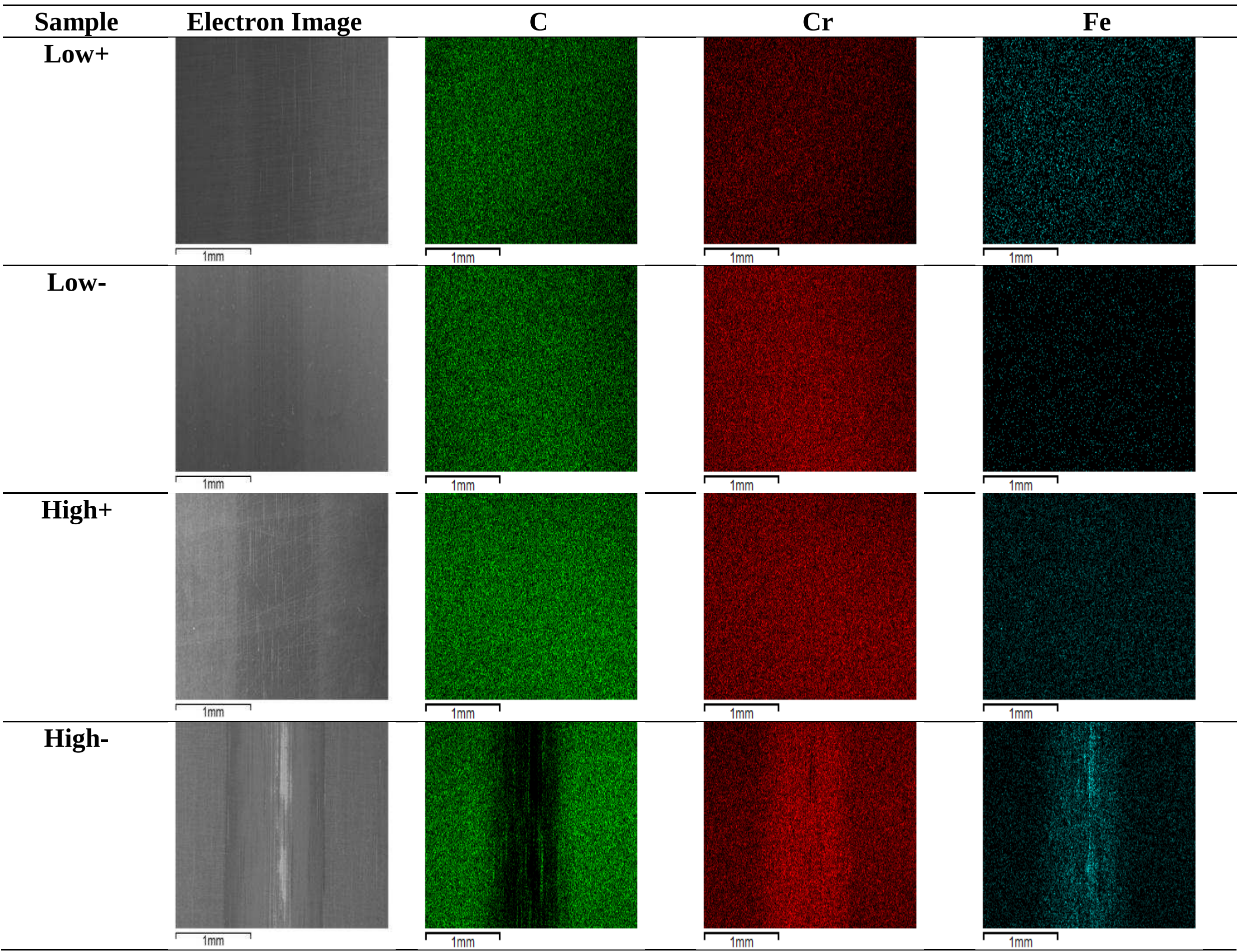

Figure 6 SEM image of a-C:15H coating along with EDX mapping of the C, Cr and Fe atoms.

It is also clear that with increasing the level of Mo-FM, Cr was richer in the middle of the wear scar than outside (higher wear). Removal of dark coating exposed the underlying bright Cr interlayer as observed by optical images and confirmed by EDX analysis. Comparing EDX mapping of C, Cr and Fe atoms of a-C:15H coating after the tests, ZDDP-containing oils with a high level of Mo-FM showed lower wear compared to ZDDP-free oils which confirms the observation from optical microscope and interferometer wear measurements of the a-C:15H coating. It should be noted that, Fe was seen to be dominant at some regions inside the wear scar for High- oil showing that either the substrate is exposed (delamination) or the coating became very thin in the wear scar region (severe wear).

The wear coefficients of the CI counterbodies for the four oils are given in Figure 7. In general, taking into account the error bars overlapping, all of the oils showed similar wear rates. Therefore, it can be argued that the different wear rates for the a-C:15H plates was not primarily due to the difference in the wear performance of the CI pin counterface and that the detection of iron only in in the wear scar using High- could not be due to the iron transfer from the pin as wear of the pin was comparable from all the tests.

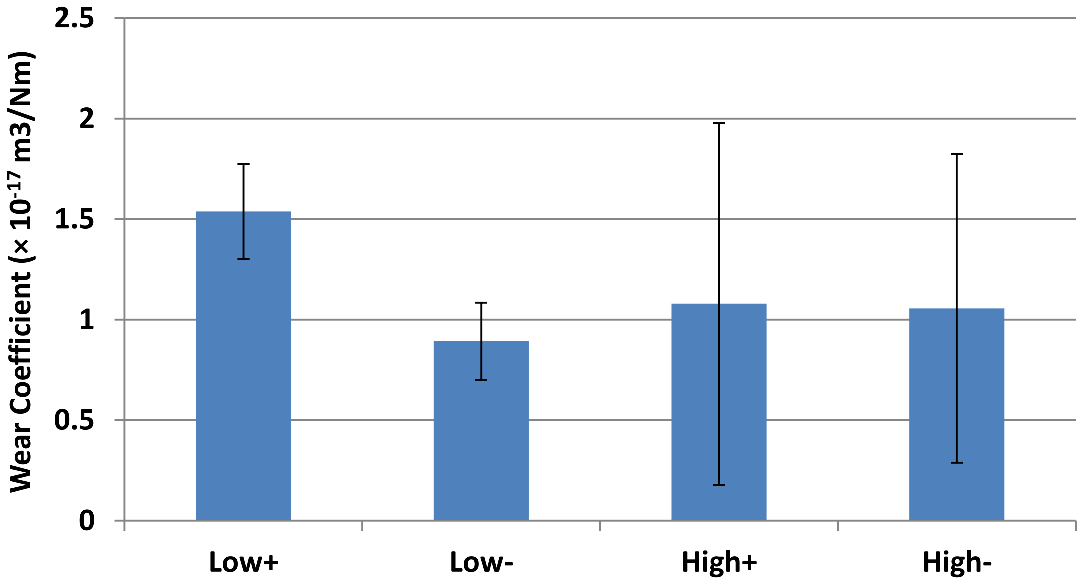

Figure 7 Dimensional pin wear coefficients as a function of lubricants for a-C:15H/CI systems

3.3 Chemical Analysis of Tribofilms

The chemical quantification of the surface tribofilms for the a-C:15H/CI tribocouple is shown in Table 4. The presence of the additive-derived elements on both the a-C:15H and the CI pin counterbody imply that the additives were decomposed under boundary lubrication and significantly influenced the tribological performance of the a-C:15H/system and particularly durability of the coating. Fe 2p peak was not detected in the tribofilm formed suggesting that delamination of the a-C:15H coating did not occur at any regions or/and that the iron coming from the pin worn particles took part in the tribofilm formation on the a-C:15H surface. Considering the fact that XPS is a more surface sensitive technique and combining these results with the observation from EDX analysis where iron was detected at some regions inside the wear track of High-, it could be argued that using High- oil; the coating became very thin (severe wear) rather than being delaminated.

Table 4 XPS quantification of tribofilms for an a-C:15H/CI system.

Sample	Surface	Elemental composition of Tribofilms (at.%)								
		Fe 2p	O 1s	P 2p	Zn 2p	C 1s	Ca 2p	Mo 3d	N 1s	S 2p
Low+	Pin	1.3	21.3	1.5	0.2	68.1	3.9	1.9	0.9	0.9
	Plate	0.0	4.3	0.3	0.2	91.9	0.8	1.1	0.9	0.6
Low-	Pin	3.8	32.4	0.0	0.0	60.7	1.1	2.0	0.0	0.0
	Plate	0.0	4.3	0.0	0.0	90.7	1.2	1.1	2.0	0.7
High+	Pin	1.2	35.7	1.1	0.2	54.9	1.8	2.6	1.8	0.7
	Plate	0.0	3.7	0.4	0.1	92.0	0.6	1.4	1.1	0.8
High-	Pin	1.6	34.9	0.0	0.0	42.7	1.3	12.3	6.4	0.8
	Plate	0.0	2.8	0.0	0.0	93.5	0.6	0.9	1.8	0.4

3.3.1 Low friction film formation

Shown in Table 4, it is also evident that the amount of Mo 3d detected on the DLC plate tribofilm formed from oils with both low and high level of Mo-FM is negligible as compared to the tribofilm formed on the pin counterpart. In addition, the amount of Mo detected on the pin tribofilm was found to be higher for high Mo-FM concentration oil without ZDDP (High-). The fitted Mo 3d peaks obtained from the High- tribofilm formed on both pin and a-C:15H coating are shown in Figure 8. Taking into account the binding energies of S 2p peaks, it is evident that the tribofilm formed on the pin contained abrasive Mo-oxide species (possible cause of DLC brittleness [19]) as well as the low shear strength MoS_2. That could explain the higher wear and lower friction obtained by the oils with a high level of Mo-FM (High-).

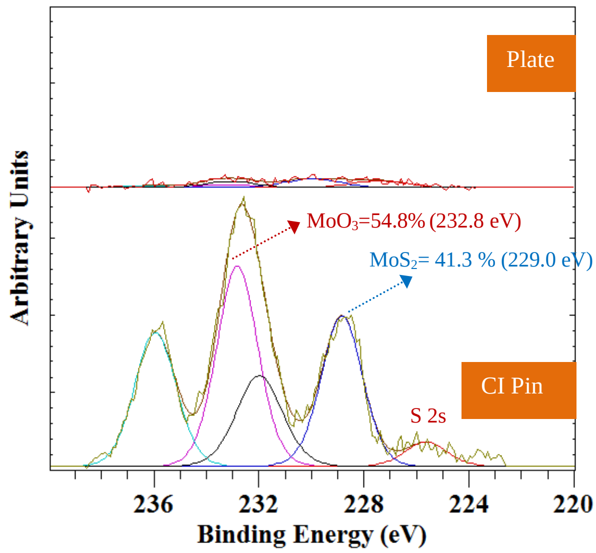

Figure 8 Curve fitting of Mo 3d peaks obtained from tribofilm formed from High- on both pin and a-C:15H coating.

The fitted carbon peaks for the highest wear giving oil (High-) in the tribofilm formed on both CI pin and a-C:15H plate are shown in Figure 9. It can be seen that only a minor portion of carbon on the CI pin was oil-derived oxygen-containing hydrocarbon species while a considerable part was detected to be pure carbon (graphitic) [28] which would derive from transfer from the coating. High wear provided by high Mo-FM concentration fully formulated oils resulted in transferring a-C:15H wear debris from the a-C:15H coating to the pin counterface which is confirmed by the presence of graphitic carbon in the tribofilms formed on the CI pin. Furthermore, the higher detected oil-derived hydrocarbon species on the CI pin could be due to the higher reactivity of ferrous counterbody with the lubricant components compared to the a-C:15H coating. Therefore, it is evident that DLC wear debris could also contribute to the friction reduction along with the additive derived low friction MoS_2 sheets [18].

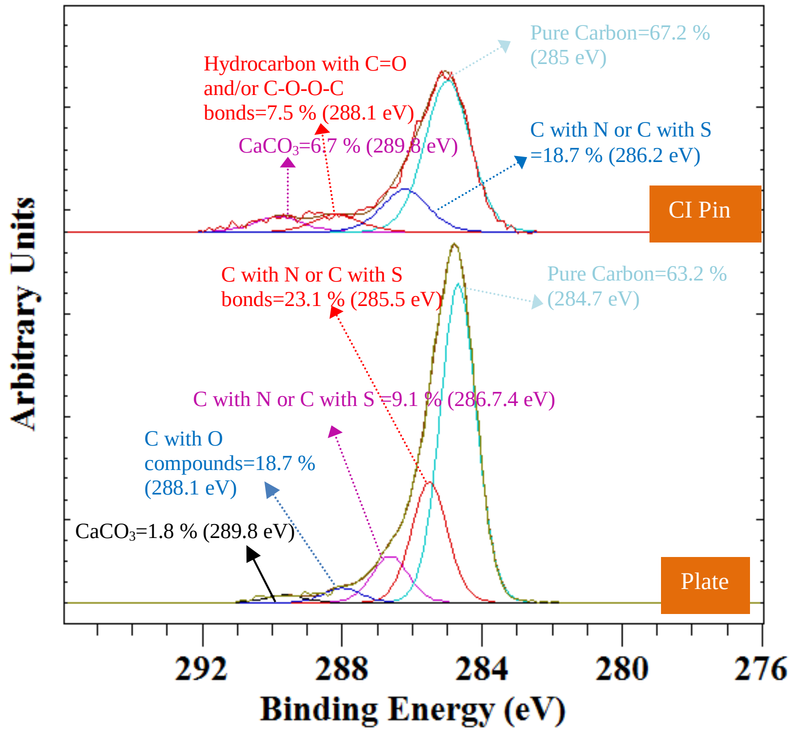

Figure 9 Carbon species on the wear scar of a-C:15H coating and CI pins for the highest wear giving lubricants (High-).

3.3.2 Antiwear film formation

The obtained results clearly show the critical role of ZDDP on the wear performance/durability of a-C:15H coating. Zn-phosphate and ZnS/ZnO species were formed in the tribofilms using all ZDDP-containing fully formulated oils which is in agreement with the presence of zinc phosphates on the low hydrogen containing DLC (a-C:15H) coating as reported elsewhere [12]. It is also clear that the presence of Mo-FM in the oil did not affect phosphate film formation on the surface. In addition, as mentioned earlier, ZDDP increased friction when added to the lubricant which is in agreement with the literature where formation of pad-like tribofilm was identified as the reason for such higher friction [29] .The fitted Zn 2p and P 2p peaks are shown in Figure 10.

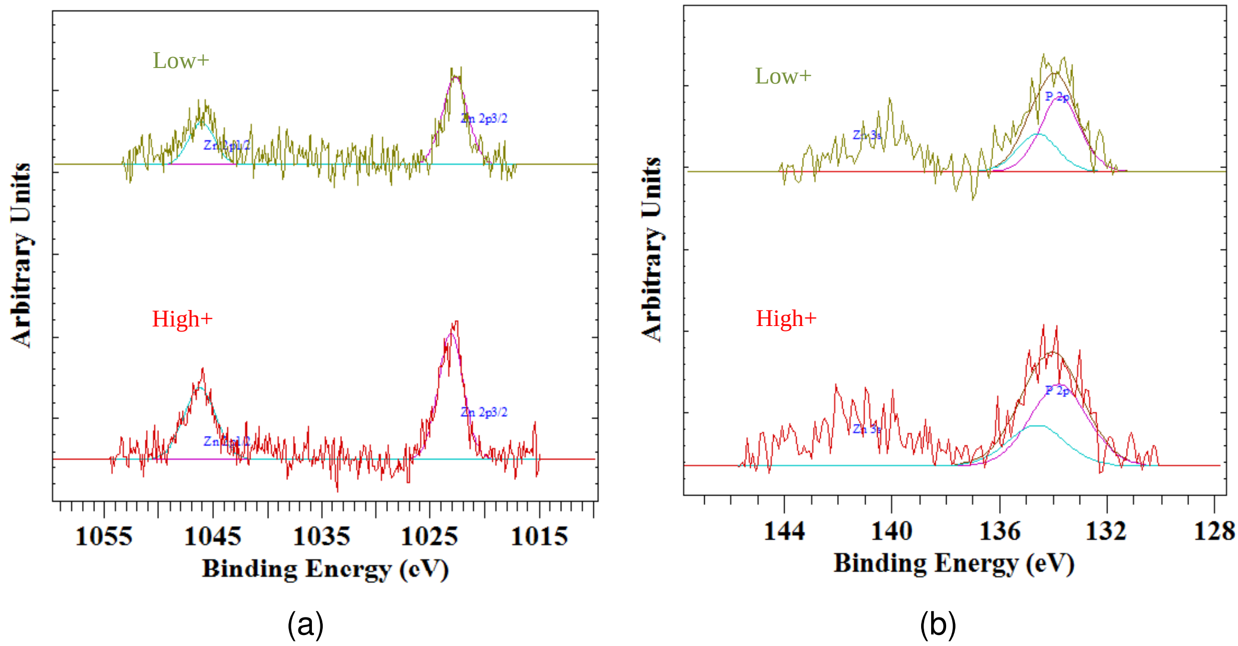

Figure 10 XPS spectra of ZDDP derived species (a) Zn 2p, (b) P2p formed on the a-C:15H coated plate using different fully formulated oils.

3.4 Mechanical properties of the coatings

Nano-indentation tests were conducted around the centre of worn a-C:15H coating surfaces. Shown in Table 5, are the hardness and reduced elastic modulus (Er) values for the coated samples after 20 hrs pin-on-plate test. Reduced modulus indicates the compliance of a sample with the indenter. It is calculated by combining the elastic modulus and Poisson's ratio of the indenter and the sample being indented. Comparing these values with properties of the as-deposited coating (H =18.6± 4 GPa and Er 180±25 GPa), it can be observed that the coatings which experienced higher wear showed decreased coating hardness and modulus of elasticity. This suggests that the mechanism of a-C:15H coating wear could be related to the change in the mechanical properties of the coating, which in turn is a function of tribochemistry of additive components on the a-C:15H coating surface. In addition, nano-indentation tests were also performed outside of the wear scar on each sample and the hardness and reduced elastic modulus values are very similar to that of as-deposited coating indicating that the wear mechanisms of the a-C:15H coatings are due to the tribological (tribochemical) processes rather than the chemical reaction of the lubricant additives with a-C:15H coating.

Table 5 Nano-scale mechanical properties of DLC coating

Sample	Maximum depth (nm)	Standard deviation (±)	Hardness (GPa)	Standard deviation (±)	Reduced elastic modulus (GPa)	Standard deviation (±)
Low+	116.2	5.5	17.2	1.8	159.1	11.5
Low-	111.5	4.7	18.2	1.7	170.6	11.3
High+	120.3	5.5	15.8	1.6	154.0	10.7
High-	70.1	12.3	14.0	1.9	148.21	11.9

4 Discussion

4.1 Effect of Mo-FM on a-C:15H coating wear

As mentioned earlier, the effect of MoDTC in increasing wear of DLC coatings has been reported in the literature [16, 18-23] however, they mainly used single additive solutions rather than more realistic fully formulated oils. Haque et al. [16, 18, 22, 23] reported this effect with MoDTC obtained from multiple sources, suggesting that this phenomenon is independent of the MoDTC molecular structure. Using fully formulated oils, this study has shown that the wear of the a-C:15H strongly depends on the level of Mo-FM in the lubricant.

An XPS study has confirmed that MoS_2 and MoO_3 which are known to be decomposition products from MoDTC [4, 5, 8] are formed particularly on the pin wear for high concentration Mo-FM-containing fully formulated oils. The nano-indentation study suggested that, depending on the level of Mo-FM in the oil, the mechanical properties of the a-C:15H coatings were modified and that the wear scar became softer than the as-received coating with increasing the Mo-FM level. It could be either due to the reaction of generated MoO_3 on the pin counterpart with the active sites of DLC (C-H bonds and dangling bonds) which could eventually result in brittleness of the coating and thus high wear [19] or the a-C:15H coating might have undergone temperature and/or stressed induced graphitisation [30-32].

4.2 Effect of Mo-FM on friction reduction

Formation of MoS_2 which are responsible for providing lower friction was mainly dominant in the tribofilm formed on the counterpart from high concentration Mo-FM-containing fully formulated oils while the amount of Mo formed on the DLC wear scar was negligible. In addition, high wear on the a-C:15H coating which was imposed by High Mo-FM containing fully formulated oils resulted in a high transfer of material to the CI pin. The presence of sp^2 carbon bonds in the DLC coating matrix provides them with inherent low friction properties and so the transfer layer of the a-C:15H coating, as evidenced by the XPS analysis, may consist of the low shear strength sp^2-dominated graphitic carbon. Therefore, it is clear that a combination of MoDTC derived MoS_2 along with DLC wear debris are governing factors in friction reduction in the a-C:15H/CI tribocouple.

4.3 Effect of ZDDP and other additives

This study also shows that ZDDP offered significant improvement in wear protection when it was used with a high level of Mo-FM (High+). Using model oil, Haque et al. [16] reported that addition of the antiwear additive ZDDP to MoDTC-containing base oil was shown to suppress the effect of MoDTC in giving high wear of DLC coating [16]. It has been shown that the high wear was not seen with DLC/DLC contact and therefore, the presence of steel counterface was thought to be crucial in promoting the formation of MoO_3[21], or iron oxide particles may produce higher local temperatures[23] which could then results in modification/graphitization of the DLC coating and thus high wear. ZDDP derived glassy phosphate species which were formed on the surface of the coating could protect the surface from excessive wear or/and formation of Iron oxide particles. ZDDP could also act as an oxidation inhibitor and hinder the formation of MoO_3 which is the potential cause of high DLC wear. Based on this study, the presence of other additives in the blend did not provide similar surface protection of the coating against "Mo-FM induced wear". Nevertheless further study is required to establish the exact link between Mo-containing friction modifiers and wear of DLC and the mechanisms by which ZDDP could stop this effect.

5 Conclusions

The following conclusions can be drawn from this study:

- High concentration of molybdenum-based friction modifier can promote wear of a-C:15H DLC coating in oils without ZDDP and this wear can be mitigated by the addition of ZDDP. However, the presence of ZDDP in the oil increased the friction.
- The mechanical properties of the a-C:15H coating can be modified by the addition of the Mo source in a fully formulated oil. Furthermore, the antagonism effect of Mo-FM to a-C:15H in terms of wear was more of tribochemistry of the rubbing surfaces rather than chemical reaction of the oils with the a-C:15H coating.
- Unlike ZDDP, the presence of other additives (antioxidants, detergents and dispersants) in a fully formulated did not provide similar protection.
- This study showed that the presence of ZDDP in fully formulated oils can promote some level of confidence that an additive solution can be tailored for the mitigation of DLC wear with formulation carrying a high level of Mo-FM (High+). However, further investigation of DLC wear induced by MoDTC is still essential.

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