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# Friction reduction mechanisms in boundary lubricated W-doped DLC coatings

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# Friction reduction mechanisms in boundary lubricated W-doped DLC coatings

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## Abstract

The applications of commercially available Diamond Like Carbon (DLC) coatings have seen a rapid increase whilst a lot of tribochemistry problems are not fully understood. This study looks into a tungsten doped hydrogenated DLC coating reciprocating against cast iron in model oils. Friction and wear of such system are then compared with steel. Raman spectroscopy is used extensively to understand the coating interactions with the lubricant/additives. Our results have demonstrated the way to characterize carbon coating structure in lubrication. It clarified the chemical decomposition of MoDTC to $MoS_2$ is the dominant process rather than the possible formation of $WS_2$ in such system. It also enbles application of in-situ tribochemical aspects using Raman spectroscopy in ambient conditions.

Keywords: DLC coating; Friction reduction and wear; Tribochemistry

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## 1. Introduction

Diamond-Like Carbon (DLC) coatings have been widely used in the automotive industry since their first introduction in 1971 [1, 2]. Some successful applications in engine components have attracted more and more attention in engineering research due to their excellent tribological properties such as low friction, wear and corrosion resistance, high hardness, high thermal and chemical stability, etc.[2]. On the other hand, stringent emission legislation has driven the development of novel lubricants with lower environmental impact. The current commercially available formulated lubricants are optimized based on ferrous materials. Most recent research has focused on the interactions between current lubricant additives and different types of DLC non-ferrous surfaces [3-11]. However, due to there being various types of DLC coatings and the complexity of additives in formulated lubricants, it is important to properly define the DLC coating and the additives in the oil. Some understanding has been provided based on experimental observations using various physical and chemical surface analysis techinques. Some questions, in particular, the tribofilm formation, decomposition of additives during the friction tests, chemical or physical adsorption, graphitization and transfer layers on the contact surfaces, have been the subject of extensive debates [3-12].

In the field of lubricant additive interactions with DLCs, previous research on lubrication of DLC coating has addressed some understandings above. Vengudusamy et al. [9, 10] carried out some tribological studies on different DLC coatings lubricated in model oils. Evidence of ZDDP-derived tribofilms formation was reported [9]. W-DLC and WC-DLC coatings suffered more wear compared to other a-C:H and a-C types coatings [9]. Study of oil containing MoDTC showed an increase in wear on the non-doped hydrogenated DLC coating due to the decomposition and chemical reactions that formed oxides and nanocrystallites [7]. Another study focused on a-C:H and a-C:Cr coatings lubricated with model oil additives. Evidence of friction reduction film formation was reported to form from the ZDDP+MoDTC-containing lubricants [8]. Molybdenum-containing lubricants showed an increase in wear for WC/C type coatings while the known friction reduction mechanisms in ferrous materials were not observed [3]. A Si-doped DLC coating was reported with no additive-derived antiwear film in short time tests of maximum one hour under boundary lubrication which the authors explained as relative chemical inertness of non-ferrous surfaces [11]. Under the mixed lubrication regime, anti-wear films could be observed [11]. Recent study of DLC coating lubricated in base oil (API Group III) was carried out by evaluating 12 different DLC coatings. W-DLC coatings suffered higher wear than other non-hydrogenated or hydrogenated coatings. Surface graphitization occurred in the tests that gave the friction reduction performance under boundary lubrication [10]. However, there is still on-going debate about graphitization and interface dangling bond interactions between the coating and lubricant additives in the tribological process. Raman spectroscopy has been applied extensively in this study by understanding ordered/disordered structures of carbonaceous materials [7, 11, 13-19]. In order to look at the carbon coating structure change, a more recent research based on TEM/EELS study has been seen in some groups in order to measure the relative carbon $sp^2$ ratio before and after the tribometer tests [20]. Understanding about GMO and DLC interactions for ultralow friction was reported and explained by some XANES and SIMS chemical analysis. The observation of negative ion $OH^-$ was explained by the mechanism of GMO degradation to generate

OH species on the friction surface[6]. However, understandings about DLC coating interactions with GMO, particularly W-DLC type coatings, are still not very clear in the literature. Not to mention the understanding of the use of these additives at reduced treat rates.

In this study, WDLC/CI tribological system is characterized by Raman Spectroscopy and Atomic Force Microscopy (AFM). An overall beneficial system of MoDTC+ZDDP solution with a friction coefficient of 0.07 is achieved. The coating carbon structure under different lubricants are studied in Raman as well as the chemical decompostion of MoDTC-containing lubricants. The decomposition product $MoS_2$ is dominant in the process rather than the possible formation of $WS_2$. The results have demonstrated the use of Raman to characterize the tribochemical process in additive-containing lubrication. This enables further in-situ study under ambient conditions.

## 2. Experiment

### 2.1 Materials and lubricants

In this study, BALINIT® C type coating (a-C: H/W) is deposited on AISI 52100 bearing steel plate by PVD process. The typical AFM image of the W-DLC coating surface topography is shown in Figure 1. The dimension of the steel plate is 7 mm×7 mm×3 mm. A reciprocating tribometer Cameron Plint TE77 (Figure 2) is chosen with a pin-on-plate configuration which represents the sliding conditions of camshaft and follower motion in a typical internal combustion engine used in passenger cars. The coated plate which represents the shim/follower is then reciprocated against BS1452 cast ion (CI) pin under lubricated conditions. The CI pin, which represents the camshaft, has a dimension of 20 mm in length and diameter of 6 mm. The sliding end has a surface of 10 mm radius. The W-DLC/CI tribometer tests are then compared with uncoated steel/CI tests results. The original material surface roughness, hardness and reduced Young's modulus are listed in Table 1 in details. Surface roughness is measured by Veeco WYKO white light interferometry. Hardness and Young's modulus are measured by Nano-indentation. Compared with literature, W-DLC coatings are slightly harder than the bearing steel but not as hard as other types of non-doped DLC coatings.

In this study, six model oils, namely from Oil A to Oil F, are chosen in order to understand the roles of individual additive tribochemical interactions during the friction tests. Details of the oils are listed in Table 2. The additives are the widely used friction modifiers (GMO and MoDTC) and anti-wear additive (secondary ZDDP) with reduced treat rates. The model oils will enable the study of single additive roles compared to fully formulated oils which contain a more complex package of additives.

## 2.2 Tribometer tests

The tests are all carried out in the testing conditions listed in Table 3. The test rig (Figure 2) program records the friction force data points every 300 seconds for duration of 2 hours. The final steady friction coefficients are calculated based on the last 30 minutes steady friction data. The initial Hertzian contact pressure simulated in the tests represents the typical operating environment in the camshaft/follower system. All tests are repeated four times for the repeatability measure.

The tests are carried out under boundary lubrication regime which is checked by the lambda ratio defined in Eq. (1).[5]

$$\lambda = \frac{effective\ film\ thickness}{surface\ roughness\ (Ra)} = \frac{h_{min}}{\sqrt{R_{q1}^2 + R_{q2}^2}}, \qquad (1)$$

where $R_{q1}$and $R_{q2}$ are the roughness of the tribological surfaces and $h_{min}$ is the minimum film thickness. The λ ratio is 0.49 for a typical test in this study which indicates that the lubrication regime is boundary lubrication ($\lambda<1$).

## 2.3 Wear measurement and surface characterization

Wear measurement is performed by Veeco WYKO white light interferometry by measuring the material volume loss on the worn plates and the diameter of the wear scar on top of the pins. The volume loss (V) of the pin materials can then be worked out by Eq. (2).

$$V = \frac{\pi h}{6}(3r^2 + h^2), \qquad (2)$$

where $h = R - \sqrt{R^2 - r^2}$, R is the sliding tip radius of the pin, r is the radius of the pin wear scar which can be worked out by the diameter measured. Thus, the diameter of the wear scar on the curved pin is a relative indication of wear that can be compared among the different lubricants.

The wear rate for both of the worn parts can then be calculated by Eq. (3).

$$V = klW, \qquad (3)$$

where k is the dimensional wear coefficient, l is the sliding distance, W is the normal load applied to the contact surface. The unit of the coefficient is $m^3N^{-1}m^{-1}$.

Surface analysis is carried out and compared by AFM (Veeco) for the topography of both W-DLC and steel surfaces in the central worn areas in contact mode for a scan area of 20 µm × 20 µm. The formation of new chemical compounds during the tribological tests and carbon coating structure study in terms of $sp^2/sp^3$ ratio were studied by Raman

Spectroscopy (InVia Raman, Renishaw). A 488 nm excitation wavelength laser source was used and two different scans were applied in this study. The first one scanned from 100 $cm^{-1}$ to 3200 $cm^{-1}$ for a full scan in order to detect chemical compound formation. Another individual scan from 800 $cm^{-1}$ to 1900 $cm^{-1}$ was performed for the carbon peaks, i.e., disorder peak (D peak) and amorphous graphitic material peak (G peak), in order to determine the carbon coating structure change during the reciprocating tests. WiRE software provided by the Raman equipment is employed for curve fitting considering full-width at half-maximum (FWMH) as constraint [21]. By fitting the G peak and D peak, the ratio of $I_D/I_G$ which is regarded as an indicator of carbon coating $sp^2/sp^3$ structure change can be calculated. A Leica optical microscope is also applied in this study to observe/compare MoDTC and ZDDP containing additives worn regions in both WDLC/CI and steel/CI tribological systems. Raman surveys of the worn regions are with the references to these images and detailed results will be discussed in the following section.

## 3. Results and discussion

### 3.1 Friction evaluation

Friction results for W-DLC/CI and steel/CI lubricated in model oils are shown and compared in Figure 3. It can be observed that GMO does not help friction reduction in neither W-DLC nor steel system. This is thought to be due to reduced amount of friction modifiers used in the test. It can be seen that single MoDTC model oil (Oil E) gives the lowest friction (0.05) in the steel/CI ferrous surface which confirms the role of MoDTC as a good friction modifier even if using a reduced treat rate. However, for W-DLC/CI, the lowest friction reduction (0.07) is given by Oil F (MoDTC+ZDDP). Single ZDDP solution (Oil B) in W-DLC tribo-system has shown a lower friction compared with steel ones in the same lubricant. Friction maintains a relatively lower value compared with ferrous based system of the same lubricant in Oil A, B, F. The presence of ZDDP in ferrous system shows a higher friction ($\mu \geq 0.10$) but in W-DLC system, the friction is reduced (Oil B and Oil F). The results of MoDTC and ZDDP containing oils have shown a great difference. This will be analyzed in the following sections.

## 3.2 Wear results

Wear results of plates and counter-part pins are presented in Figure 4 and Figure 5, respectively. The depth profile measurement by WYKO has shown that some of the coatings that lubricated with certain oils cannot survive for the 2 hour tests. This is the case for base oil without additive (Oil A), and single friction modifier containing oils (Oil C and Oil E). Previous study has indicated that some non-doped hydrogenated DLC coatings showed an increase in wear in oil containing MoDTC [7]. Although W-DLC coating carbon films are removed in Oil A, C and E, the friction is not reduced to the friction of steel surfaces (Figure 3 and Figure 4). It is believed that the carbon films have been removed in these cases as the depth of the wear scar exceeded the carbon coating thickness. However, interlayers still exist in these cases. This will be discussed in the surface analysis section later; the presence of ZDDP effectively protects the coating. Regarding the wear rate of coated and uncoated steel plates, Oil E gives an overall low friction and wear on both surfaces in the ferrous system. However, W-DLC/CI showed an overall lower friction and lower wear (both pin and plate) when lubricated in Oil F whilst the single solution of MoDTC generates high wear on the coating surface. It is interesting that there is an overall beneficial effect of ZDDP/MoDTC additives when used together in WDLC/CI tribo-pair. However, this is not the case with the combination of ZDDP/GMO containing oils in the same tribo-pair. The wear coefficients are in a similar range ($*10^{-18}m^3N^{-1}m^{-1}$) in the cases where the coating still survives. Test duration is 2 hours, thus the focus of this study is the friction reduction mechanisms provided that both steel and W-DLC tribo-systems have similar low wear. Whether the well-known mechanisms of MoDTC friction reduction [4, 22] applies in W-DLC/CI tribo-system as well as whether there is possible interaction between tungsten dopant and additive elements will be further analyzed physically and chemically in the following sections.

### 3.3 Physical nature of tribofilms

In order to understand the physical topographic nature of different additive interactions on the W-DLC surfaces in relation to their different tribological friction and wear performance, AFM is employed for the selected samples as is shown in Figure 6. In the steel/CI tests with ZDDP-containing lubricants (Figure 6 (a), (b) and (d)), the surface topography images are quite different. Friction is relatively high ($\mu \geq 0.10$). It is thought that the presence of ZDDP could form phosphate films which will increase friction as a consequence. This is in agreement with the studies widely reported for ZDDP films. The lowest friction in the ferrous system is given by single friction modifier MoDTC (Oil E) which shows a different topography in Figure 6 (c). In W-DLC/CI tests, the coating gets protected by ZDDP from the wear results whilst showing different topography images (Figure 6 (e) and (f)) and different friction coefficients. These indicated that the friction performance depends on the surface topography of the films formed on the coating surface.

The friction and wear results have shown a great difference between steel/CI tribo-system and WDLC/CI tribo-system for Mo-containing oils. AFM images have shown the small area of the wear scar regions. The overall wear scar physical nature of the films in correlation with friction and wear knowledge of MoDTC can be studied by the optical microscope. Figure 7 shows the 3D optical images of the wear scar regions lubricated in Oil E (MoDTC) and Oil F (MoDTC+ZDDP) in both WDLC and steel systems, respectively. The ferrous based tribo-pair has an almost invisible wear scar on the counter-part pin (Fig. 7(a) circled) of Oil E. It can be seen clearly this gives the lowest friction and wear of all the test results. The introduction of ZDDP to MoDTC containing oil shows clearly that the both of the plate and pin surfaces have surface coverage which is different from the MoDTC single solution (Fig. 7 (a)-(d)). Also, this combined formulation doesn't show friction reduction whereas single MoDTC gives lowest friction. The steel plates in both oils are in a similar range of wear (Fig.7 (b) and (d)). On the other hand, the single MoDTC solution generates severe wear on both pin and W-DLC coated plate surfaces (Fig. 7 (e) and (f)). The wear measurement results by the interferometer shows the depth of the wear scar on the plate exceeds the carbon film thickness which means the coating cannot survive for the 2 hours test in this case. The introduction of ZDDP helps the W-DLC coated tribo-pair with a manageable wear (Fig. 7 (g) and (h)) which shows friction reduction ($\mu$=0.07) compared to the steel/CI tribo-pair ($\mu$=0.10).

Based on the above understandings, some post-test roughness analysis of the wear scar properties are presented in Table 4. The ZDDP-containing oils maintain a little smoother surface on the coating compared with its original WDLC coating roughness. However, the counterpart surfaces, which are cast iron with original roughness about 0.1-0.2 μm, have become much smoother (Oil B 0.07 μm, Oil D 0.08 μm, Oil F 0.04 μm). It should be noted that Oil B and Oil D give different friction results with similar surface roughness but different AFM topographic surfaces, which means the friction behavior again depends more on the chemical nature of the tribofilms. It should be noted that Oil F which gives the overall friction and wear performance has actually ended up with an even smoother surface. This is thought to be the effect of MoDTC added to the ZDDP solution.

It is obvious that more understanding about the chemical nature based on the above physical nature of the Mo-containing films needs to be carried out. The next section will discuss the chemical surface analysis in detail with reference to the images in Figure 7.

### 3.4 Tribochemical nature of films and coating structure analysis

AFM images have evidenced the existence of different surfaces formed in the reciprocating process. Optical images have shown the difference between MoDTC and ZDDP-containing lubricants. The combined ZDDP+MoDTC model oil has formed a relative smoother tribo-pair in the W-DLC coated system. This section will show the chemical nature of these surface films. Raman spectroscopy is used extensively in this study by taking surveys of a wide coverage of the wear scar regions in correlation to Figure 7 images. The typical spectra of the wear scar lubricated in Oil E and Oil F on both ferrous and non-ferrous tribo-pairs are shown in Figure 8. The spectra outside the wear scars of steel and W-DLC coated plates are also collected as a reference.

The Raman signal of $MoS_2$ can be studied in the Mo-containing lubricants. Three of the four first-order Raman active modes could be studied, i.e., $E_{1g}$, $E^1_{2g}$ and $A_{1g}$ [15, 23]. $E^2_{2g}$ could not be observed here due to cut off of the Rayleigh filter (start point at 100 $cm^{-1}$) [15, 23, 24]. Here, $E_{1g}$, $E^1_{2g}$, $A_{1g}$ and $E^2_{2g}$ refer to phonons associated with vibration of the layers, either S-Mo-S layer, or adjoining rigid layers [15, 24]. In the ferrous system, both steel plate and cast iron counter-part pin have some iron oxides contents as shown in the 800 $cm^{-1}$ Raman shifts. The appearances of $MoS_2$ are shown in both Oil E and Oil F under the ferrous system. However, Oil E shows the lowest friction (0.05) whereas Oil F has a relatively higher one (0.10). The friction reduction mechanism of MoDTC is widely reported which is believed to be the formation of $MoS_2$ [15, 24]. $MoS_2$ has the weak Van der Waals forces between the sliding layers which makes it a good solid lubricant. The presence of ZDDP may interfere with this mechanism, i.e., the formation of ZDDP films, even if the formation of $MoS_2$ still exists during the process. Compared with the microcrystalline $MoS_2$ sample [15, 24, 25], the peaks that centered about 408 $cm^{-1}$ ($A_{1g}$) and 383 $cm^{-1}$ ($E^1_{2g}$) show strong intensity. A weak peak of $MoS_2$ centered about 450 $cm^{-1}$ can also be observed in steel plates in both Oil E and Oil F (Fig. 8 (a)). The indication of $MoS_2$ formation is clear. The carbon peaks (centered in the range from 1300 $cm^{-1}$ to 1600 $cm^{-1}$) in Fig. 8 (a) of Oil E on the pin wear scar is probably due to residual lubricant although the post-test samples are rinsed in heptane to remove excess oil.

When talking about sulphur-containing additives lubrication in the specific DLC coating system, i.e., W-DLC coating used in this study, there is also possibility of the formation when tungsten could interact with sulphur. Some recent study fabricated a sulfurized W-DLC coating lubricated in MoDTC oils [26]. The formation of WSx is reported by the authors which helps friction reduction. Back to talk about the tests in this study where no pre-treatment was carried out for the W-DLC coating itself but sulphur-containing additives exist in the model lubricants, Raman study about the possible formation of $WS_2$ can also be carried out. For references of Raman spectra of $WS_2$ [24, 25], $E_{1g}$, $E^1_{2g}$ and $A_{1g}$ of $WS_2$ can also be studied, i.e., 306 $cm^{-1}$ ($E_{1g}$), 356 $cm^{-1}$ ($E_{2g}$), and 421 $cm^{-1}$ ($A_{1g}$). Based on the single crystal references, it is clear that none of these phonons associated with W-S vibration mode can be observed clearly in Raman spectra collected in the wear scar region. Thus formation of $WS_2$ is not a dominant process compared with formation of $MoS_2$ in such a lubrication system. This is different from the self-lubricated mechanism suggested by Wen et al [26]. And it is possibly due to the chemical state of tungsten in W-DLC coating is in its carbide form which is difficult for chemical attack by other molecules.

W-DLC coating lubricated in Oil F gives an overall beneficial tribological performance (Fig. 3-5). It can be seen in Figure 8(b) that on the coating surface, $MoS_2$ layer was formed. However, film formation of ZDDP on W-DLC coating surface is showing less effect on the $MoS_2$ friction reduction mechanism because the friction behavior of WDLC/CI and steel/CI are quite different although they lubricated in the same oil with the same $MoS_2$ formation. It also gives an overall smoother tribo-pair as is discussed in Section 3.3. Thus gives an overall beneficial tribological performance in Oil F in the coated system. There is no indication of $MoS_2$ formation on the wear scar surface in Oil E but a strong appearance of oxides material (centered around 800 $cm^{-1}$) on the surface where the carbon films are removed. For the high wear Oil E, there is no carbon transfer material residual on the counter-part pin whilst carbon materials are still appearing on the coated plate. This is thought to be the carbon film residuals within the interlayers. The W-DLC type of coating has some interlayers of less than 0.5 micrometer as is stated in the coating specification. The various friction results of the coated plates lubricated in Oil A, C and E where the carbon films are removed are thought to be the interactions of the additives and coating interlayers/disordered carbon residuals.

The spectra are carefully collected with consideration of laser power; all the spectra are collected using 10% of the total laser power. Thus the counts generated indicate a semi-quantitative comparison of the $MoS_2$ and $MoO_3$ coverage of the selected Raman spectra. The spectra in Figure 8 are all shifted in parallel for clarifying any overlap of the two spectra. Previous study has shown that in tribological tests in the air atmosphere, the formation of $MoO_3$ and oxides is responsible for the failure of $MoS_2$ lubrication [15, 22]. Compared with the $MoO_3$ powder Raman spectrum [15], no clear bands in 158 $cm^{-1}$, 285 $cm^{-1}$, 666 $cm^{-1}$ and 995 $cm^{-1}$ in steel/CI system for Oil E and F but strong Raman band in 820 $cm^{-1}$ region of the oxides materials. The study of the ratio of $MoS_2$ to $MoO_3$ is reported by previous study, indicating a higher ratio results in a better friction reduction of the overall system [4, 22]. Thus the friction reduction mechanism can be explained that the amount of oxides formed on the surface was not significant compared with the stronger appearance of $MoS_2$ layers. It can be concluded that MoDTC will form mainly $MoS_2$ in the wear scar in the ferrous system.

However, it is reported that W-DLC type coating generally suffers from more wear in MoDTC-containing lubricants [9, 10]. This is possibly due to the formation of $MoO_3$ that resulted in such high wear [7]. In W-DLC/CI Raman spectra for Oil E and Oil F, 820 $cm^{-1}$ band indicates formation of $MoO_3$ and other iron oxide materials. Oil E shows significant amount of oxides materials in the W-DLC coating system. The presence of

ZDDP again modifies the tribological interface with a higher $MoS_2$/Oxides ratio (Oil F). The study of Mo-containing additives interactions in DLC coatings is reported by previous research [4, 7] with high wear. It is possible that the wear of W-DLC coating is also the formation of $MoO_3$ on the worn surface. This is because such oxide formation is due to the chemical decomposition process by the lubricant additive rather than purely depending on the test surfaces.

The carbon coating structure can be studied by Raman spectroscopy with a static scan of the first-order carbon peak area. Again, the spectra are collected with a 10% of the total laser power in all the sampling regions; the higher the laser power, the deeper it goes to the coating surface. However, a laser power of typically over 50% will result in laser induced carbon coating damage of all the chosen W-DLC coatings both inside and outside of the wear scars. The W-DLC coating chosen in this study has a tungsten interlayer. The tungsten-interlayer Raman spectra can be observed with high laser power whilst lower laser power will not penetrate over 2 µm (DLC film thickness). Care should be taken to perform Raman studies on the coating structure analysis. The well-known Raman spectrum for carbon G band (around 1580 cm-1) is referred to $E_{2g}$ phonon of $sp^2$ bonding. It is due to all $sp^2$ sites. The disordered band, D band (around 1350 $cm^{-1}$), is referred to the phonons of $A_{1g}$ symmetry [14, 16]. D peak refers to only six-fold rings[27]. A good feature of Raman for visible photons is that although W-DLC coating contains hydrogenation within the process, it doesn't show the C-H bonds[27]. Generally, the smaller of $I_D/I_G$ intensity ratio can indicate lower disorders of graphitized structures [16, 27]. The post-test sample $I_D/I_G$ intensity ratios are presented in Table 4. It only shows the results in the presence of ZDDP (Oil B, D and F) which the carbon coatings still exist after the tests. In single friction modifier oils, W-DLC coating could not survive for the duration of the 2 hour tests, hence they are not applicable here for the coating structure study. The ratio is a relative indicator of the carbon coating structure for the surface. Oil D (GMO+ZDDP) shows no significant change compared with the original W-DLC coating whilst Oil B (ZDDP) and Oil F (MoDTC+ZDDP) contain more $sp^2$ disordered content on the coating surfaces. In these two oils, friction reductions are achieved. However, Oil D, which the carbon structure of the coating doesn't seem to be changed, has its friction increased. All these lubricants are ZDDP-containing with/without friction modifiers. Friction and wear results have not shown a clear linkage regarding the carbon structure change. This indicates that graphitization only happens in selected lubricants during the tribometer tests. Friction reduction of Oil F is probably due to both the formation of $MoS_2$ and graphitization. Oil B friction reduction is probably due to the change in DLC coating structure (an increase in $sp^2$ content) which is ZDDP induced. All these results also indicate that the friction performance in these model oils depend on the lubricant additives interactions with the coating although graphitization happens in some model oils (additive induced graphitization).

### 3.5 The roles of conventional friction modifiers and ZDDP in W-DLC/CI tribological system

It is obvious from the Raman study that there exists the formation of layers on the ferrous and non-ferrous coatings on the interfaces (Fig. 8). The question of whether these layers are formed from the counter-part CI pins and then transferred to the W-DLC surfaces is still not clear. However, in all cases, both the pin and plate materials have a good coverage of similar surfaces, either $MoS_2$ rich (Fig. 8(a) Oil E, F and Fig.

8(b) Oil F) or oxides rich (Fig. 8(b) Oil E). In other words, it is the case of high ratio of $MoS_2/MoO_3$ surface formation or low ratio surfaces. Some DLC against DLC interface tests may be desired to further clarify the question of film formation and film transfer.

Single friction modifier model oils led to premature failure of the tungsten-doped DLC coatings. W-DLC coatings are very reactive with the single friction modifier/base oil lubricants. However, GMO significantly reduced friction for hydrogen-free DLC coatings as was reported previously. The studies by Topolovec-Miklozic et al. showed GMO helped the friction reduction on hydrogenated coatings by varying the speed of MTM test rig [8].They claimed that low speed does not greatly reduce boundary lubrication friction. Explanation of GMO in friction reduction at intermediate speeds was due to the formation of thin reacted or adsorbed layers on the solid surfaces with high viscosity. However, at slow speeds in boundary lubrication, friction reduction did not seem to be significant. Another study which discussed about the super low friction by a steel/DLC tribo-pair ($\mu$=0.02) and DLC/DLC tribo-pair ($\mu$=0.03) lubricated in GMO solution (1 wt%) was reported due to the tribofilm rich in OH-terminated carbon surface[6]. In this study, GMO did not function properly on the W-DLC coating which is thought to be due to the lower additive concentration limiting proper additive function.

By introducing ZDDP into the single friction modifier containing oils, the combined model oils can effectively improve the wear performance of the coating. This is a clear message that ZDDP forms protective layers on the interface. However, Raman study has not shown any significance of the ZDDP-induced film formation in the spectra. The surface roughness maintains a similar level to the original coating surface in the presence of ZDDP-containing lubricants in W-DLC/CI system. However, the friction behaviors are quite different. Tribological performances of the W-DLC/CI system highly depend on the additives.

## 4. Conclusions

- The combination of ZDDP and MoDTC shows good friction reduction and wear protection for W-DLC/CI tribo-system under the test conditions. The presence of $MoS_2$ in the interface is the major contribution of the overall friction reduction and the use of ZDDP reduces the wear to a manageable lower level compared to the ferrous system. Friction reduction is contributed by both formation of $MoS_2$ and surface graphitization.
- Raman spectroscopy has demonstrated to be a useful technique to characterize the chemical decomposition of MoDTC-containing lubricants. This enables further study on in-situ characterization in ambient conditions.
- Although tungsten content appears in the coating as dopant, the formation of $MoS_2$ by chemical decomposition from MoDTC is dominant in such system rather than the possible formation of $WS_2$.

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## Figure Captions

Fig. 1. AFM image of the original W-DLC coating surface

Fig. 2. Configuration of TE77 pin-on-plate reciprocating tribometer

Fig. 3. Friction coefficient comparisons between W-DLC coating and steel in model oils

Fig. 4. Friction vs wear of the plate lubricated in model oils

Fig. 5. Friction vs wear of the counter part pin wear in model oils

Fig. 6. Selected AFM wear scar images of steel and W-DLC coated plates lubricated in model oils

Fig. 7. Optical images of the wear scar regions

Fig. 8. Raman spectra of Steel/CI tribopair (a) and W-DLC/CI tribopair (b) in Mo-containing oils - Oil E (MoDTC) and Oil F (MoDTC+ZDDP)

## Table Captions

Table 1 Material properties of the original test samples.

Table 2 List of model oils.

Table 3 Experiment conditions.

Table 4 The post-test wear scar properties in ZDDP-containing lubricants.

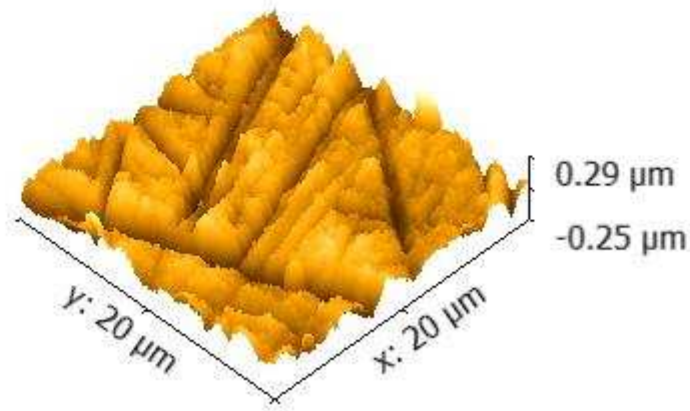


**Fig. 1.** AFM image of the original W-DLC coating surface

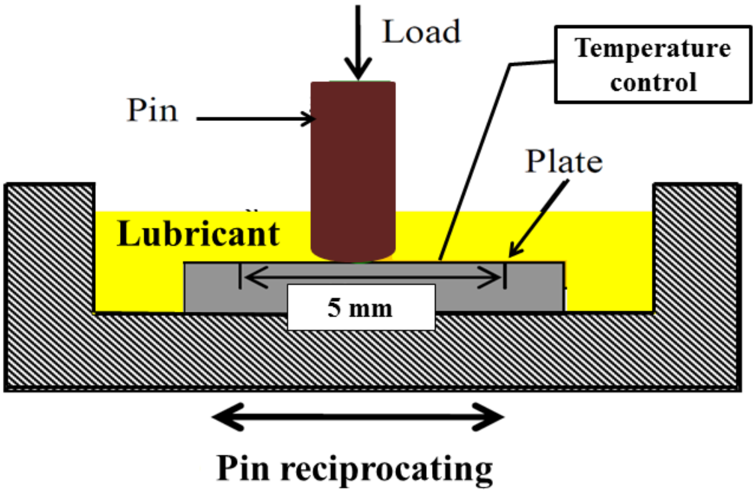


**Fig. 2.** Configuration of TE77 pin-on-plate reciprocating tribometer

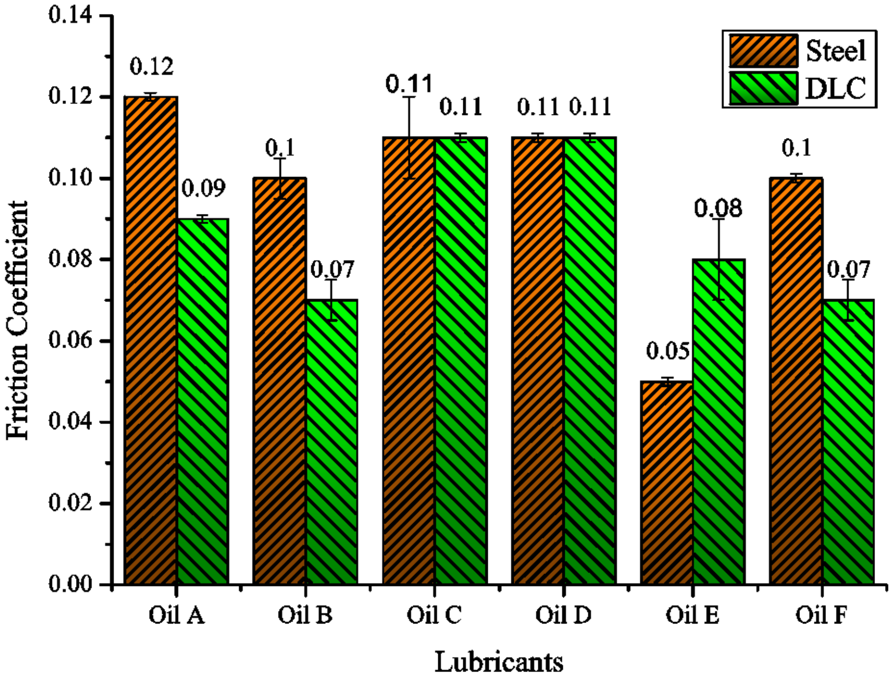


**Fig. 3.** Friction coefficient comparisons between W-DLC coating and steel in model oils

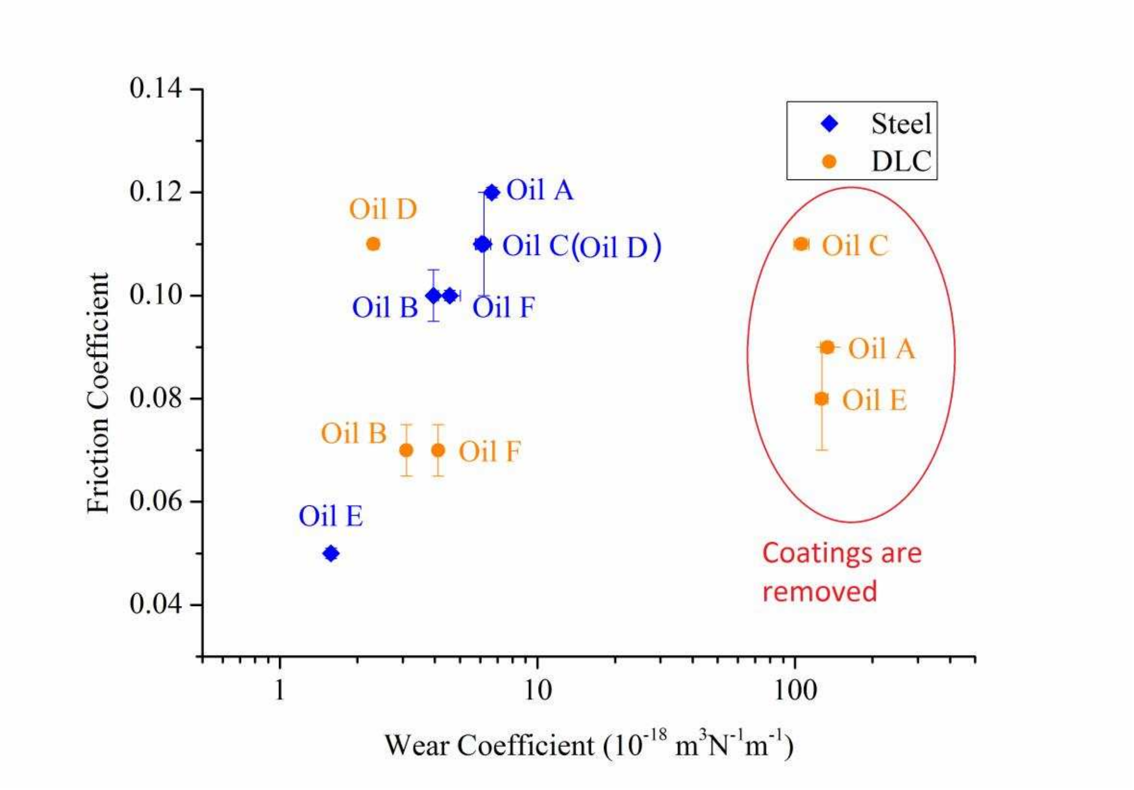


**Fig. 4.** Friction vs wear of the plate lubricated in model oils

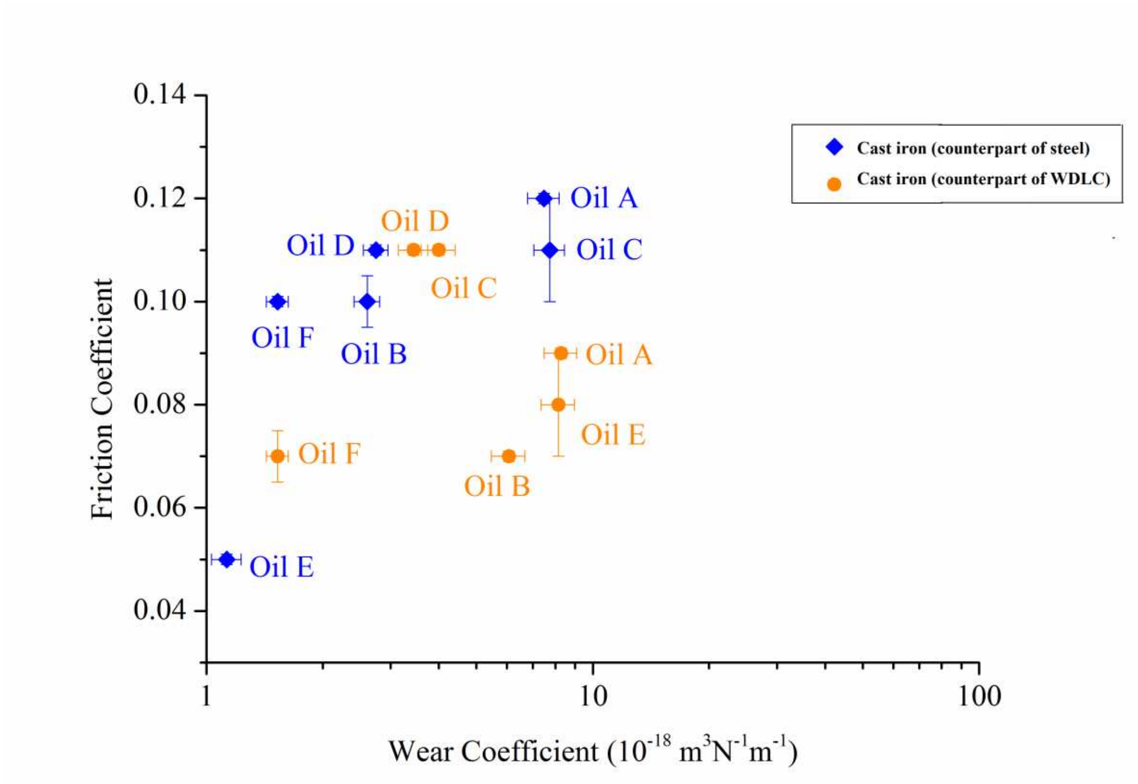
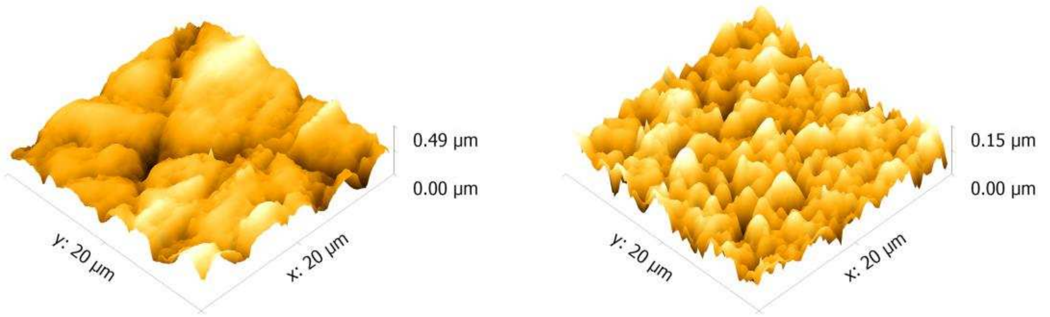
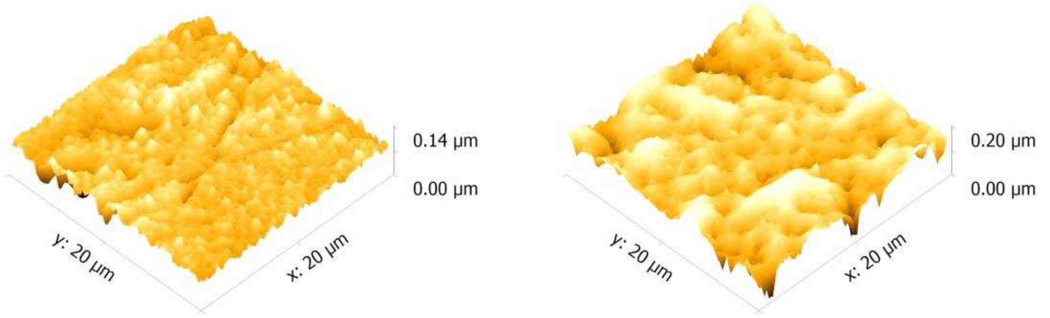


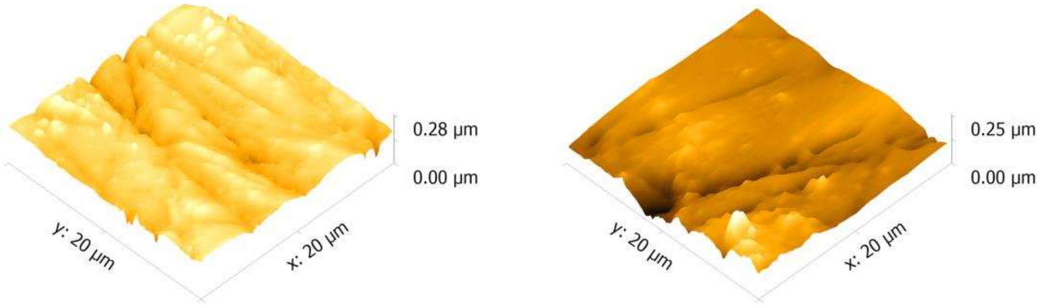
**Fig. 5.** Friction vs wear of the counter part pin wear in model oils



(a) Steel Oil B Base Oil+ZDDP (b) Steel Oil D GMO+ZDDP



(c) Steel Oil E Base Oil+MoDTC (d) Steel Oil F MoDTC+ZDDP



(e) DLC Oil D GMO+MoDTC (f) DLC Oil F MoDTC+ZDDP

**Fig. 6.** Selected AFM wear scar images of steel and W-DLC coated plates lubricated in model oils

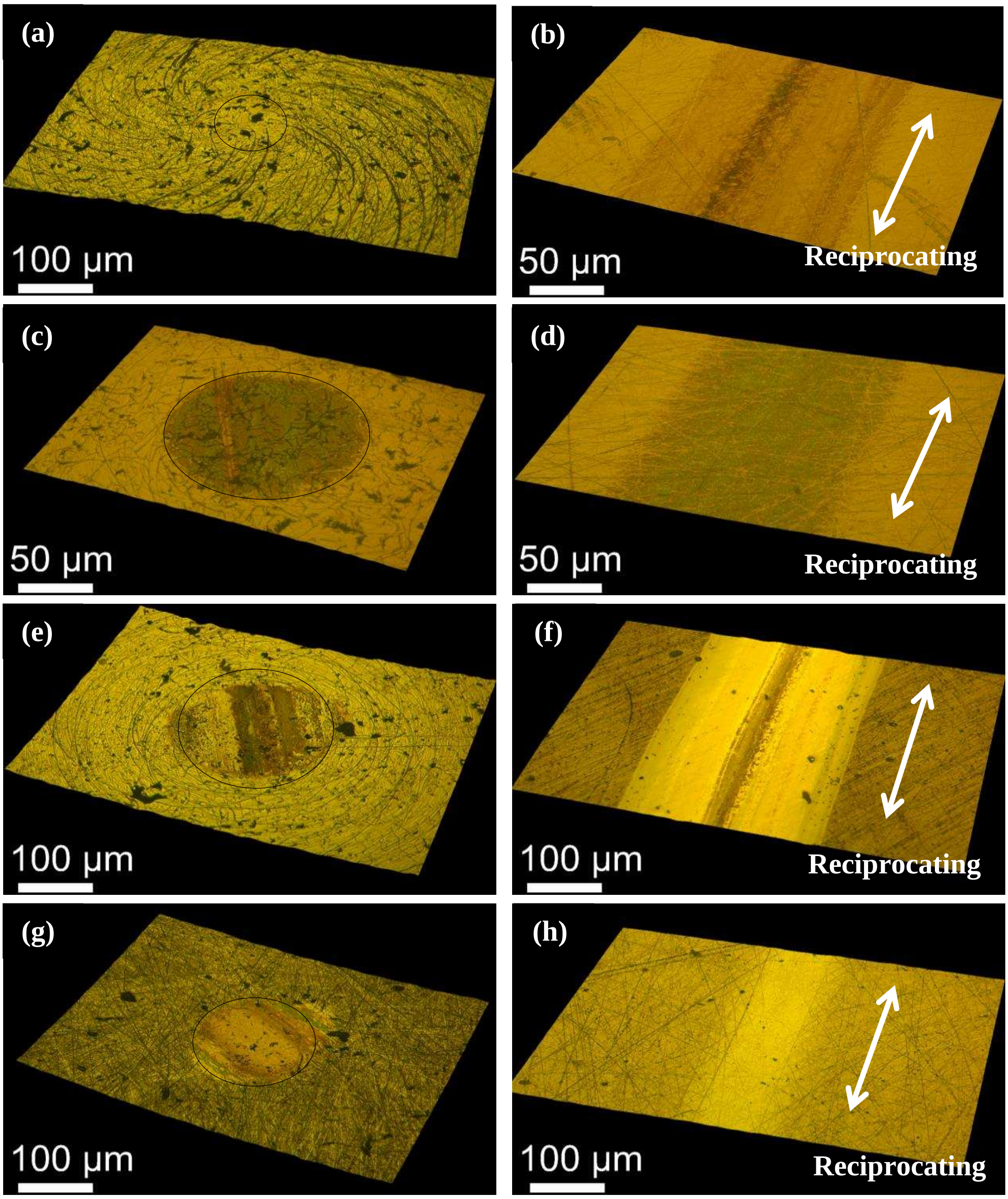


**Fig. 7.** Optical images of the wear scar regions – (1) Steel/CI tribopair in Oil E pin (a) and plate (b); (2) Steel/CI tribopaire in Oil F pin (c) and plate (d); (3) W-DLC/CI tribopair in Oil E pin (e) and plate (f); (4)W-DLC/CI tribopair in Oil F pin (g) and plate (h)

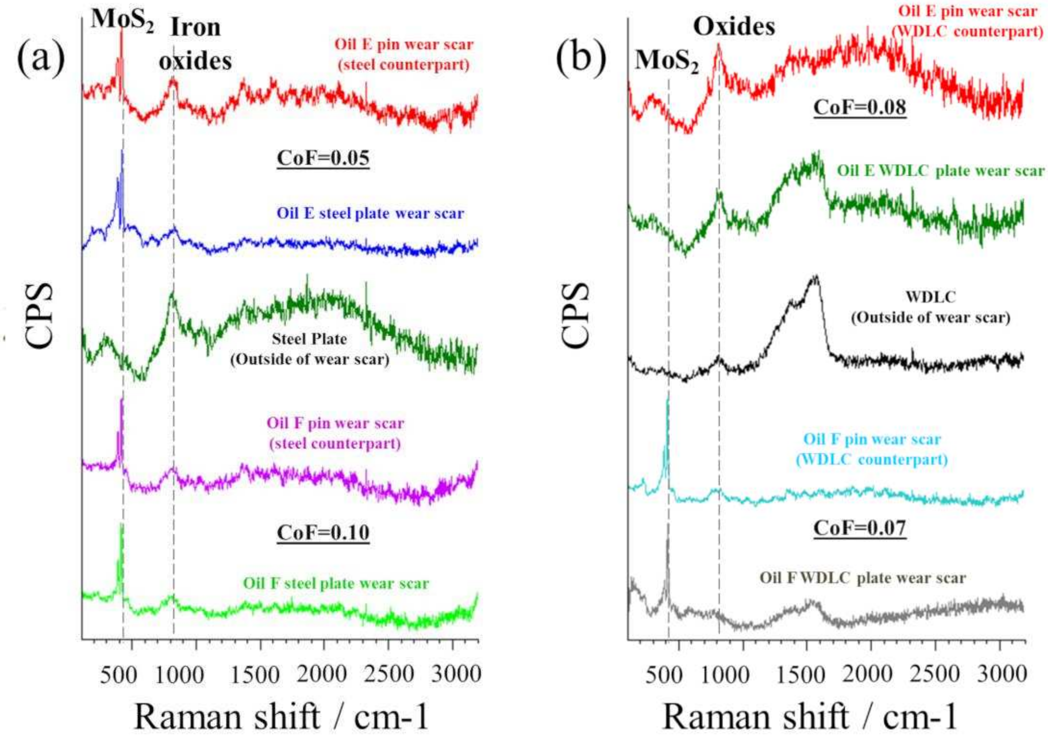


**Fig. 8.** Raman spectra of Steel/CI tribopair (a) and W-DLC/CI tribopair (b) in Mo-containing oils - Oil E (MoDTC) and Oil F (MoDTC+ZDDP)

**Table 1**
Material properties of the original test samples.

| Parameter | Steel | W-DLC coating | Cast iron |
|---|---|---|---|
| Standards | AISI52100 | AISI52100(Substrate) | BS1452 |
| Type of coating | - | W-DLC (BALINIT ® C*) | - |
| Hardness | 6.1±0.8 GPa | 8.7±1.9 GPa | 4.6±0.5 GPa |
| Atomic % of hydrogen | - | 15% | - |
| Coating thickness | - | 2-3 µm | - |
| Reduced Young’s modulus | 187±13 GPa | 119±18 GPa | 148±24 GPa |
| Roughness, $R_q$ | 0.03-0.05 µm | 0.03-0.05 µm | 0.1-0.2 µm |

[*] Commercially available from Oerlikon Balzers Coating UK Ltd.

**Table 2**
List of model oils.

| Oil[*] | Additive Type | Treat rate/wt% | Viscosity@100˚C/Pa*s |
|---|---|---|---|
| Oil A | - | Base Oil | 0.0026 |
| Oil B | ZDDP | 0.08% P | 0.0032 |
| Oil C | GMO | 0.2% | 0.0031 |
| Oil D | GMO+ZDDP | 0.08% P | 0.0028 |
| Oil E | MoDTC | 100 ppm Mo | 0.0029 |
| Oil F | MoDTC+ZDDP | 0.08% P, 100 ppm Mo | 0.0028 |

[*] Base oil of the model oils are all Poly-alpha olefin Group IV base stock (PAO 4).

**Table 3**
Experiment conditions.

| | Conditions |
|---|---|
| Load | 25 N |
| Stroke | 5 mm |
| Frequency | 25 Hz |
| Initial Hertzian contact pressure | 600 - 700 MPa |
| Lubricant temperature | 100 ˚C ± 5 ˚C |
| Test duration | 2 hours |

**Table 4**
The post-test wear scar properties in ZDDP-containing lubricants.

| Sample | I (D) / I (G) ratio | Friction coefficient μ | Coating Wear /$10^{-18} m^3 N^{-1} m^{-1}$ | Coating Roughness/μm | CI Roughness/μm |
|---|---|---|---|---|---|
| DLC Original | 1.07 | - | - | 0.03 | - |
| Oil B | 1.00 | 0.07 | 3.10 | 0.02 | 0.07 |
| Oil D | 1.06 | 0.11 | 2.31 | 0.02 | 0.08 |
| Oil F | 1.04 | 0.07 | 4.12 | 0.02 | 0.04 |