



UNIVERSITY OF LEEDS

This is a repository copy of *Effect of Lubricant Additives on the WDLC Coating Structure When Tested in Boundary Lubrication Regime*.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/86636/>

Version: Accepted Version

---

**Article:**

Yang, L, Neville, A, Brown, A et al. (2 more authors) (2015) Effect of Lubricant Additives on the WDLC Coating Structure When Tested in Boundary Lubrication Regime. *Tribology Letters*, 57 (14). 1 - 12. ISSN 1023-8883

<https://doi.org/10.1007/s11249-015-0464-y>

---

**Reuse**

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

**Effect of lubricant additives on the WDLC coating structure when tested in  
boundary lubrication regime**

**Liuquan Yang<sup>a\*</sup>, Anne Neville<sup>a</sup>, Alisdair Brown<sup>b</sup>, Paul Ransom<sup>b</sup> and  
Ardian Morina<sup>a</sup>**

<sup>a</sup> **Institute Functional Surfaces (iFS), School of Mechanical Engineering, University  
of Leeds, Leeds, LS2 9JT, UK**

<sup>b</sup> **Afton Chemical Limited, London Road, Bracknell, Berkshire, RG12 2UW, UK**

**\* Corresponding author: Tel: +44 113 343 2085. E-mail: mnly@leeds.ac.uk (L.  
Yang) and [Liuquan.Yang@oerlikon.com](mailto:Liuquan.Yang@oerlikon.com).**

**Effect of lubricant additives on the WDLC coating structure when tested in  
boundary lubrication regime**

L. Yang<sup>a\*</sup>, A. Neville<sup>a</sup>, A. Brown<sup>b</sup>, P. Ransom<sup>b</sup> and A. Morina<sup>a</sup>

<sup>a</sup> Institute of Functional Surfaces (iFS), School of Mechanical Engineering, University  
of Leeds, Leeds, LS2 9JT, UK

<sup>b</sup> Afton Chemical Limited, London Road, Bracknell, Berkshire, RG12 2UW, UK

**Abstract**

Improvements of coating deposition technology enable the mass production of high quality Diamond-Like Carbon (DLC) coatings at an industrial scale and also increase their use in lubricated contacts. However, the understanding of the interactions of different lubricant additives with this material is not yet fully developed. This study focuses on several fundamental aspects of the tungsten-doped DLC coating (denoted as WDLC) behaviour under boundary lubrication conditions with model lubricants. The effect of lubricant additives on the coating structure change is discussed in terms of carbon structure and the tungsten dopant. Electron Energy Loss Spectroscopy (EELS), XPS and Raman spectroscopy characterization for the upper carbon layers indicate that the WDLC coating interacts chemically with selected lubricant additives. The study provides information on both coating and additive optimization under boundary lubrication.

**Keywords:** DLC coating; lubricant additives; EELS

---

\* Corresponding author. **Now at Oerlikon Metco.**

Tel.: +44 113 343 2085

E-mail address: mnly@leeds.ac.uk (L. Yang) ; [Liuquan.Yang@oerlikon.com](mailto:Liuquan.Yang@oerlikon.com)

## 1. Introduction

The increasing demand for lower fuel consumption aligns with the aim to reduce carbon emissions. The stringent emission legislation has pushed forward research and has accelerated the introduction of hard coatings such as DLC and nitride coatings [1-5]. Application of DLC coatings in the automotive industry is seen as an alternative approach towards reducing the dependence on some high SAPS (Sulphated Ash, Phosphorus and Sulphur) additives [1, 6]. This is due to their relative chemical inertness compared with ferrous surfaces. However, more and more research has shown the dependence of additives on tribological performance [2, 6, 7]. There are numerous commercially available DLCs which differ from each other by their different carbon structures [5]. On the other hand, commercial lubricants comprise different additives and also depend on selected interfaces. Understanding of coating and additive interactions requires more fundamental research to understand how optimization of the entire system can be achieved [1, 6-8].

There are some key questions that need to be answered. In particular, the understanding of additive interactions on coating surfaces, and how the coating structure changes chemically and/or mechanically remains largely unknown. This study focuses on only one coating (**W-doped Diamond-Like Carbon -WDLC**) lubricated with model lubricants. This coating is commercially-available and has been extensively investigated. However, reported literature showed no superior performance over other metal-doped or non-doped DLCs [1, 6, 7, 9-11]. There are a number of possible reasons, i.e., different coating composition, hydrogenation, tribological and processing

conditions, and the various additive packages used [1, 7, 11]. Most of the literature is on large scale experimental evaluations. Tribochemistry understanding between WDLC coatings and lubrication additives is limited.

A lot of work has been done on different mechanisms of some most popular and conventional additives in ferrous and non-ferrous (DLC) surfaces, such as Glycerol Mono Oleate (GMO), Molybdenum DiThioCarbamate (MoDTC), Zinc DialkylDithioPhosphate (ZDDP), etc.[1, 2, 6-10, 12-14]. Most of them suggest that the mechanisms are either by interactions with the carbon coating surfaces (GMO for example) [9, 10, 15], or chemical decomposition (MoDTC and ZDDP for example) [2, 14], or formation of tribological films that claimed to have some superior structure or properties [7, 13]. Some of the mechanisms suggested by experimental results have also found evidence in molecular dynamic simulations [10, 13, 16]. However, the WDLC coating has not been clarified yet with those mechanisms. The change in the coating structure in different lubricants has been studied in the last 20 years with the aim being to clarify the potential for graphitization and the possible relationship with friction, wear and durability of DLC coatings [9, 12, 17]. The relationship between mechanical properties of the coating interface and different additives is still not yet clear although recent work has started to deal with aspects of this [8].

Starting from an understanding of the WDLC coating structure, this study investigates the effect of additives on the change of the coating structure. Surface analysis techniques are employed to assess both the physical (Atomic Force Microscopy - AFM, Scanning Electron Microscopy - SEM and Nano Indentation) and chemical (Raman Spectroscopy, Electron Energy Loss Spectroscopy - EELS and X-ray Photoelectron Spectroscopy - XPS) properties of both the tribofilm and the potential

structure change of the coating. The outcome of this study is expected to provide **valuable** information on lubrication system design and optimization when using transition metal-doped coatings and lubricant additives.

## **2. Experimental Methodology**

### 2.1 Materials and lubricants

WDLC coating is deposited on an AISI 52100 bearing steel coupon with a thickness of around 2.5 micrometres with some chromium interlayers. The coating used in this study is metal doped and a hydrogenated coating. Details of the original coating can be found in Figure 1 **which shows the** Transmission Electron Microscopy (TEM) image of the coating cross-section. Full information of the coating is listed in Table 1. **The process of the deposition for the WDLC coating does not use oxygen containing precursors. Therefore, oxygen is not a constituent of the as-deposited coating.**

Lubricants used in this study are the combinations of three conventional additives, i.e., GMO, MoDTC and ZDDP. These additives were blended in base oil (PAO 4). Details are shown in Table 2. They are: Oil 1 (Base oil), Oil 2 (ZDDP), Oil 3 (GMO+ZDDP), Oil 4 (MoDTC+ZDDP) and Oil 5 (GMO).

### 2.2 Tribological tests and wear measurements

The tests are conducted using the Cameron Plint TE77 with a **point contact** pin-on-flat configuration. In these tests, an initial contact pressure 700 MPa is simulated with a 5 mm stroke. A WDLC coupon is clamped and immersed in a temperature controlled lubricant oil bath at 100 °C. The counter-part pin is BS1452 cast iron (CI) with a sliding

end of 10 mm in radius. The test duration is 2 hours and final steady friction coefficient is calculated by averaging the last 30 minute friction data points.

Measurement of the wear volume of the coating material loss is carried out using a Bruker NPFLEX white light interferometer. From these data the wear coefficients are calculated. Prior to wear measurement, samples are cleaned in acetone in an ultrasonic bath for 15 minutes to remove possible films, deposits and/or contaminated species that could skew the measurement of the coating material loss.

### 2.3 Surface characterization

A Veeco DI SPMLab NT Atomic Force Microscope (AFM) is used to study the surface topography by the contact mode scan for an area of  $5\ \mu\text{m} \times 5\ \mu\text{m}$  in the wear scar region. The samples are cleaned in n-heptane to remove the excessive oils.

Chemical characterization is studied by X-ray Photoelectron Spectroscopy (XPS), using a VG Escalab 250 (Thermo Scientific) model with a high intensity monochromatic Al K-alpha soft X-ray source. By monitoring the spectra of W 4f, top surface (several nanometers) are analyzed, in particular, if additives would interact with the W dopant. Prior to this analysis, samples are rinsed in n-heptane for a couple of seconds. **The data are processed by CasaXPS (CasaXPS software version 2.3.15 Ltd., UK).**

The effect of additives on the carbon coating structure change in terms of  $sp^2/sp^3$  ratio is studied and compared in two different ways, i.e., micrometer scale Raman spectroscopy (InVia Raman, Renishaw) and nanometer scale electron energy loss spectroscopy (EELS). Prior to both studies, the samples are cleaned in n-heptane **with the aim to remove only the excessive oil from the surface**. A 488 nm laser source is

used in wear scar surfaces by scanning from  $800\text{ cm}^{-1}$  to  $1900\text{ cm}^{-1}$  in Raman. Under this visible laser excitation, two carbon peaks can be studied. Proper curve fitting is performed considering the full-width at half-maximum (FWHM) [3].

EELS is conducted by using a Philips CM200 TEM system. Both carbon K-edge core loss and low loss spectra of the cross-sectional interfaces are collected. The EELS provides a precise way to measure carbon  $\text{sp}^2$  content at the spatial resolution at nanometre scale. A platinum electron beam protective layer is deposited on the surface. Thus the contamination and coating structure damage by the powerful ion beam can be reduced. By curve fitting EELS spectra, the  $\text{sp}^2$  content can be quantified and compared with highly ordered pyrolytic graphite (HOPG) as a reference (100%  $\text{sp}^2$ ). The spectra collecting angle is 6 mrad in consideration of the orientation effect. This makes sure that the EELS measurement of HOPG has no issues caused by the mutual attraction of polar molecules resulting from alignment of dipoles.

A nano indentation platform, NanoTest<sup>TM</sup> (Micro Materials Ltd) is employed with a fixed load (2 mN) - fixed time (loading/unloading for 30 seconds, respectively) method. Prior to nano-hardness measurements, the samples are cleaned in acetone bath. Mechanical properties, i.e., hardness and Young's modulus of WDLC coating, are measured. A matrix of  $10 \times 5$  indentation data points are collected, starting from the edge of the wear scar, to the wear scar centre with an interval of  $35\text{ }\mu\text{m}$ . Thus a more representative average hardness/modulus result covering a wide range of the worn region can be studied and compared with the original WDLC surface. Post-test unloading curves are analyzed by the Berkovich equation as the rig uses a Berkovich diamond indenter. A typical indentation of the coating is shown in Figure 2. Depth, hardness and reduced modulus of the coating surface are calculated. The proposed



method chosen in this study shows an indentation depth less than 200 nm (less than 10% of the total coating thickness), indicating the measurements are taken from the coating only without any effect from the substrate.

### **3. Results**

#### **3.1 Friction and wear**

Processed friction and wear results of the lubricated interfaces for the five model oils are presented in Figure 3. WDLC has a large range of friction (the highest 0.10; the lowest 0.06), indicating the significant role of additives in WDLC/CI lubrication. In base oil, WDLC friction is reduced compared with steel/CI tests (friction coefficient 0.12). Considering that there are no additives in base oil, the difference in friction between steel/CI and WDLC/CI tribo-systems is due to the intrinsic properties of the coating. The presence of the conventional anti-wear additive ZDDP in different model oils results in huge differences although the same ZDDP treat rate is applied. Both ZDDP and MoDTC+ZDDP solutions give low friction (0.07); ZDDP+GMO solution shows an increase (0.10). ZDDP is commonly used as an anti-wear additive and friction has been widely reported to increase due to the formation of the phosphate tribofilm on steel contacts in the literature [7].

A previous study on DLC coatings lubricated in GMO has indicated that the frictional surface generates OH-terminated surfaces (a few nanometres) and graphitic layers which would lead to a significant friction drop [10]. This is a phenomena referred to as superlubricity. However, a study by the authors previously using one GMO solution (0.2 wt%) in WDLC coating has shown removal of such DLC coating [14]. In the

current study, the lowest friction observed at the WDLC/CI interface is 0.06 (GMO, 0.5 wt%). The mechanism needs to be clarified and compared. In the literature, the coatings used for the superlubricity studies were mostly hydrogen free, non-doped DLC coatings against steel/DLC counter parts [9, 10]. The widely reported literature on WDLC coatings normally reports moderate friction with sometimes high wear depending on selected additive systems [1, 7, 11]. The structure of WDLC coating is quite different to non-doped DLC as is mentioned in Figure 1, i.e., the coating grows above interlayers with tungsten carbide and amorphous carbon sources alternating every a few atomic layers. The commonly-used DLC coatings are more amorphous (mixed carbon structures) rather than such a layered composite. **The potential friction reduction mechanism for the layered-like WDLC coating will be discussed further in this study, taking into account the coating properties obtained by Raman and EELS.**

Wear for short laboratory scale test of 2 hours is expected to be low and reduced compared to steel due to the increase in hardness. However, in these conditions, the coating lubricated with a base oil fails. A depth profile of the wear scar shows over 2.5  $\mu\text{m}$  from the centre, indicating a complete removal of the carbon film. The additives in this paper, whether traditionally categorized as anti-wear agents or friction modifiers, protect the coating surface and reduced the wear coefficient compared to base oil. However, tests in the single additive MoDTC system carried out in another study, resulted in the coating being worn out completely after very short periods [14]. The lubricant additive interactions on WDLC-lubricated systems have shown great importance. **The coating structure and interactions in boundary lubricated conditions are investigated by AFM, XPS, Raman and EELS in this study.**

### 3.2 Physical nature of the tribofilm – an AFM and SEM study

Effect of additives on the coating wear was studied by AFM topography. Figure 4 shows the small wear scar area topography of  $5\ \mu\text{m} \times 5\ \mu\text{m}$  in comparison with the original WDLC coating. The vertical direction is the reciprocating sliding direction. The first message is that the reciprocating process ‘polishes’ the surface. The coating maintains manageable wear for short time (2 hours) tests in the presence of additives. Thus the oil chemistry plays an important role in WDLC lubrication. However, completely different topography is produced by different additives. As a result, the lubrication system exhibits different friction values whilst the direct relationship between topographic images and lubricant additives are not clear.

An SEM image of WDLC coating lubricated in base oil is presented in Figure 5. It can be seen that polishing wear of the WDLC coating is continuously removing the coating surface and delamination has occurred (black spots). The presence of lubricant additives does prevent the coating from severe wear, indicating again the importance of lubricant additives in WDLC coating lubrication. However, no direct relationship can be concluded from the AFM and SEM studies in terms of friction and wear, and their relationship to the topography. Therefore, other physical properties, such as the upper coating layer mechanical hardness and elastic modulus of the wear scar, will be discussed in the next session.

### 3.3 Physical nature of the upper carbon layers – a Nano Indentation study

Figure 6 results clearly show that mechanical properties of surface layers of WDLC coating also depend on the additives used in the tribological system. Hardness and modulus of the worn region in base oil are also measured although the carbon films are

removed in places. It can also be seen in Figure 6 that organic friction modifier GMO influence WDLC coating structure with both hardness and reduced modulus decreased (GMO+ZDDP and GMO).

The presence of ZDDP increased the hardness in the absence of GMO. The pressure induced surface hardening indicates the anti-wear film is more compliant than the underlying coating surface [13]. Regarding the change in elasticity of the materials, it is normally attributed to the changes in the chemical connectivity[13]. GMO changes the coating structure in a way physically/chemically as is suggested in the previous discussions. The degree of reduced modulus of the worn regions decreased to 120 GPa (GMO+ZDDP/GMO) compared with original coatings (140 GPa). It is believed that a highly cross-linked structure increases the modulus of the material [13]. Thus the ZDDP and ZDDP+MoDTC containing lubricants normally show an increase in hardness. However, hardness change in GMO-containing lubricants modifies the surface in a completely different way, i.e., there appears to be a significant loss in hardness on the very top surface layers. In other words, the tribofilms formed on the surface have shown great differences in mechanical properties and additive dependence. Reduction in hardness may also benefit the counter-part where its nature is originally cast iron. Such soft surfaces without any anti-wear film formation can result in high wear.

The increase in hardness and modulus for MoDTC+ZDDP containing lubricants can be explained by the highly cross-linked chemical connectivity of the lubricant additives in the tribofilms [13]. It is widely reported that cross-linking anti-wear film formation and the synergy of MoDTC+ZDDP play an important role in friction and wear reduction [2, 13]. Hardness of DLCs lubricated in MoDTC containing lubricants in recent literature shows a good agreement due to surface hardening [8].

### 3.4 XPS – A study on the doping element W

WDLC coating does have a high wear (Figure 3) in base oil but this wear has seen to be reduced depending on the lubricant used. Whether tungsten carbide interacts with lubricant additives is not yet understood. XPS W 4f spectra of the post-test samples are shown in Figure 7. It should be noted that apart from W 4f spectrum, the XPS analysis has included also the spectra of other elements detected on the wear scar. However, the primary focus for the current study is the understanding of the tungsten structure qualitatively hence only W 4f spectra have been shown. For the ones with minimum wear on the coating, the dominant features of the  $4f_{7/2}$  and  $4f_{5/2}$  spectra are metallic (W/WC) [17-20], with binding energy (B.E) =31.5 eV (W $4f_{7/2}$ ). In the presence of ZDDP/MoDTC additives, there is also a possible interaction between tungsten and sulphur species, i.e., the formation of WS<sub>2</sub>. For binding energy at about B.E = 32.8 eV (W $4f_{7/2}$ ), there is also a possible formation of WS<sub>2</sub> [19, 21] that overlapped with the tungsten oxides. The clarification of the formation of WO<sub>x</sub> and WS<sub>2</sub> is necessary. Study of similar tribofilm by using Raman spectroscopy [14] has enabled clear identification of WS<sub>2</sub> and MoS<sub>2</sub> in the tribofilm. With/without MoDTC, the wear scar of ZDDP sulphur-containing samples are also checked by Raman spectroscopy with the same procedure discussed in the previous study. There are no Raman spectra in the range of 350cm<sup>-1</sup> to 420 cm<sup>-1</sup>, indicating there is no formation of WS<sub>2</sub> on any of the worn surfaces without MoDTC [14, 22, 23]. Only in the combination of ZDDP/MoDTC oil has shown strong Raman peaks centered about 408 cm<sup>-1</sup> and 383 cm<sup>-1</sup> in agreement with authors' previous study [14]. These peaks indicate the formation of MoS<sub>2</sub>. Therefore, the rise of the chemical states of tungsten shown in Figure 7 is mostly attributed to the

oxidation of tungsten, rather than sulphurization. These indicate no dramatic changes in coating metallic structure.

The presence of additives (GMO, MoDTC and ZDDP) on the coating surface gives rise to oxidized tungsten  $4f_{7/2}$  and  $4f_{5/2}$  spectra ( $WO_3/WO_2$ ) [17-20]. It is clear there is a level of oxygen integration into the tribofilm on the coating surface which means the coating dopant is interacting with the lubricant additives. The W 4f peak features an even stronger oxide appearance where the oil is additive-free (only hydrocarbon chains). The coating fails as is shown in its wear measurement. Introduction of ZDDP additive to such a WDLC/CI tribological system has reduced the formation of tungsten oxides. ZDDP helps to control the level of oxygen adsorbing on the lubricated surfaces leading to, as current results suggest, less tungsten oxide formation on the coating surface. The formation of tungsten oxides in base oil tribology tests may possibly be the reason for the high wear (coating failure). Thus controlling the level of oxygen in the WDLC/CI tribological system appears to be critical and is primarily responsible for different friction and wear performance.

### 3.5 Raman spectroscopic study on the coating structure and the related tribological performance

Whether the carbon structure has been changed with its carbon atom hybridization, or in other words, whether the  $sp^2/sp^3$  content has changed, has been studied using Raman spectroscopy by qualitative analysis of the carbon  $sp^2$  content. Raman spectroscopy analyzes across a micrometre scale domain in depth from the top surface. Spectra are collected using 10% of the total laser power as is discussed in a previous study [14].

The calculation of  $I_D/I_G$  ratio for carbon D peak and carbon G peak involves peak fitting for the Raman spectra of the carbon region. The peak fitting considered the D band at  $1350\text{ cm}^{-1}$  (Phonons of  $A_{1g}$  symmetry) and G band  $1580\text{ cm}^{-1}$  ( $E_{2g}$  phonon of carbon  $sp^2$  bonding). A good feature of Raman for visible photons (compared with UV Raman) is that although WDLC coating contains hydrogenation within the process, it does not show the C-H bonds [3]. Thus the ratio of  $I_D/I_G$  intensity gives an indication of the extent of disorder in graphitized structures [3]. Following a number of approaches (background removal, data normalization, and curve fitting) with the software of the spectrometer, the results are then comparable from a qualitative aspect. Results are shown in Figure 8 with a plot of  $I_D/I_G$  ratio against friction coefficient for each lubricant, respectively.

The  $I_D/I_G$  ratio of the original WDLC coating (prior to any tribology testing) is also provided in the graph and a virtual value of zero for friction coefficient is assigned. The ratio dropped compared with the original coating structure in the cases of low friction (GMO, ZDDP, and ZDDP+MoDTC), indicating a lower degree of disorder in graphitized structures. In other words, the carbon content at a particular spot size has more  $sp^2$  content. This is in an agreement with other reported literature about the change in carbon structure [9, 12, 14], i.e., coating re-hybridization. However, the frictional performance cannot be simply linked to the change between post-test  $I_D/I_G$  ratio and the ratio without lubrication (original coating). This is obvious as the rank of the change of  $I_D/I_G$  ratio is  $\Delta(\text{ZDDP-WDLC}) > \Delta((\text{MoDTC+ZDDP})\text{-WDLC}) > \Delta(\text{GMO-WDLC})$ , whilst the rank of the friction coefficient is  $\mu(\text{ZDDP}) = \mu(\text{MoDTC+ZDDP}) > \mu(\text{GMO})$ . Furthermore, the little rises in GMO+ZDDP containing lubricant results in a higher friction.

The Raman spectroscopy study of additive-induced layers gives us the non-quantitative understanding of the surface structure under a large domain (typically at micrometre scale). The advantage of this technique is that all the experiments can be done in an ambient environment rather than in high vacuum conditions. However, the tribochemistry and effect of additives on the tribological performance and/or the coating structure seem to be difficult to be studied by this length scale. This is because as is discussed in section 3.3 of the nanoindentation, the mechanical properties change of the upper layers has several hundred nanometres and the tribochemistry of different additives can only be studied if the tribofilm and/or coating structure has significant big change that can be analyzed by Raman at a micrometre scale. To enable the fundamental study of interactions between additives and coating atoms, EELS is introduced as a semi-quantitative method to study the carbon bonding tribochemistry.

### 3.6 EELS – A semi-quantitative study of coating $sp^2$ content of the cross-sectional interface

EELS measures the change in kinetic energy of electrons after they have interacted with the sample. It gives structural and chemical information about a solid with an energy resolution up to 0.1 eV. Different elements have distinct EELS spectra and this technique has been used for many years for material characterization [4, 24, 25]. There are mainly two different features for the same element showing in an EELS spectrum, the core loss and low loss, depending on the different energy band. With the care of curve fitting in both spectra at a wide range of energy losses, EELS can determine the type of atoms and the numbers of atoms of the element of interest [4, 24]. For DLC coating, carbon can be easily detected and thus it offers a good way of semi-quantifying



the carbon  $sp^2$  content of the carbon materials and compares the tribochemistry. The coating surface is examined at the nanometre scale.

TEM samples of the cross-sectional area in the wear scars have been prepared similar like what is shown in Figure 1. Carbon materials exhibit two EELS featured spectra for distinguished features about different chemical bonding, core loss (main loss region over 250 eV) and low loss (less than 100 eV). Both core loss and low loss spectra in correlation to Figure 1 (EELS interface and EELS bulk) are collected, aiming to investigate the coating carbon structure change between the top surface of the wear scar (interface) and the area close to the interface (bulk, adsorption). Different from the study of carbon structure by Raman spectroscopy which studies a surface area with a submicron depth, EELS study on carbon low loss spectra (Figure 9 of WDLC coating for example) and carbon K-edge core loss spectra (Figure 10 of WDLC coating for example) is on a thin cross-sectional film in the wear scar region with nanometre resolution.

By mathematical data processing and normalizing to a reference, the  $sp^2$  content of the carbon coating can be quantified. Here highly ordered pyrolytic graphite (HOPG) is used as a reference (pure  $sp^2$ ). There are publications suggesting ways to process EELS data, claiming advantages and drawback of the methods [4, 5, 24]. Zhang et al [4] suggested a three Gaussian's peak fitting for the core loss; Daniels et al [24] suggested the data processing for low loss. Both methods are used in this study for the core loss and low loss spectra collected, respectively. Both these papers considered the possible contribution of C-H  $\sigma^*$  in their method [4, 24]. As a significant degree of hydrogenation is maintained in the original WDLC coating structure, the method suggested by Zhang et al [4] for three Gaussian's fitting method is chosen.

For low loss (Figure 9), mathematical processes are applied and two carbon coating features can be further measured. One feature centered at ca. 6.5 eV, is defined as the interband transition of  $\pi \rightarrow \pi^*$ . The bulk valence Plasmon centered at 26 eV features the  $(\pi + \sigma)$  contents [24]. These overlapped features can then be quantified in a way by measuring the content of  $sp^2$  ( $\pi \rightarrow \pi^*$ ) using a 4 eV window onset at 4.5 eV and a 60 eV window (most of the inelastic intensity) onset from the same position.

For the core loss data, a series of background removal, three Gaussian's fittings, and  $sp^2$  content measurement of asymmetric peak centered at ca. 285 eV ( $1s \rightarrow \pi^*$ ) and total of 20 eV window (main carbon structure) onset at 282.5 eV are applied. Three Gaussian's peak fitting considers carbon C=C  $\pi^*$  at ca. 285 eV (red in Figure 10), C-C  $\sigma^*$  at ca. 292 eV (green) and C=C  $\sigma^*$  at ca. 300 eV (orange) [4]. The equation for  $sp^2$  quantification with reference to HOPG is shown in Eq.1. The processed data are tabulated in Table 3. Overall, the core loss data show the interfaces of the coatings after the tests have higher  $sp^2$  content except for MoDTC+ZDDP oil. Low loss data varies from case to case. The residual of GMO peak is quite different from the others. There are also differences between Raman and EELS studies as are suggested by Figure 8 and Table 3. All these observations will be discussed in discussion section.

$$sp^2\% = \frac{\left( \frac{I_{sp^2}}{I_{total}} \right)_{sample}}{\left( \frac{I_{sp^2}}{I_{total}} \right)_{HOPG}} \quad (\text{Eq.1})$$

## 4. Discussion

### 4.1 Monitoring carbon coating structure – Raman vs. EELS

Both Raman and EELS have been employed for material characterization with great success [3, 24, 25]. From the material characterization point of view, they represent different length scales, i.e., Raman at a micrometre scale and EELS at nanometre scale. Single additive Oil 5 (GMO) and Oil 2 (ZDDP) show good agreement between EELS core loss and Raman analysis which support the Raman experiment results in a positive way that the coating surface experienced an increase in  $sp^2$  content due to the additive. However, EELS study of the other two additive-containing oils does not fully correlate to the Raman study. Oil 4 (MoDTC+ZDDP) gives a good friction reduction (0.07) and the surface is not significantly changed into rich  $sp^2$  content according to EELS study; Raman study gives an indication that, on a larger and deeper domain,  $sp^2$  content has increased. On the other hand, Oil 3 (GMO+ZDDP) shows an increase in  $sp^2$  content in EELS analysis (and friction increased) but not in agreement with the same trend in Raman study. From the results sections, it is clear that the effect of lubricant additive formulation will lead to different tribological friction and wear performance. The mechanical properties change at the upper coating layers is also measured (Figure 6). Effect of additives on coating structure is likely to be considered by the EELS measurement if tribochemistry of the tribofilm is the primary target for such investigation rather than a general material characterization.

It should be noted that Raman fitting results shown in Figure 8 with the method described earlier are repeatable by 1 decimal place (1 d.p.). At least five static scans in different areas of the wear scar are collected and fitted. Thus the values in Figure 8 are comparable as they are collected by the same condition and the same processing method. Possible reasons for the differences between EELS and Raman are as follows. Firstly, different length scales of Raman and EELS would affect these measurements. The

measurement would correlate only when the wear regions are largely dominated by the additive induced graphitization process and homogenous films are formed. AFM images have shown clearly that ZDDP-containing lubricants have relatively rough (not uniform) surfaces after the tests, particularly MoDTC+ZDDP and ZDDP. Furthermore, MoDTC+ZDDP lubricant gives a good friction reduction (0.07) which may also be attributed to the widely accepted mechanism, i.e., formation of MoS<sub>2</sub> [2]. In a smoother surface (GMO in Figure 4), both Raman and EELS core loss show a good agreement.

The study here has shown Raman cannot be implemented solely for the study of the coating structure change by different lubricant additives due to the length scale of Raman. Fundamental understanding of carbon re-hybridization, dehydrogenation, and chemical bond scissions can be investigated with techniques such as EELS. In this study, the following discussions will be focused on the EELS measurements.

## 4.2 EELS study on friction and coating structure

Both EELS and Raman are historically used to characterize the carbon based materials [3, 4, 24, 25]. The bulk material properties can be easily investigated by Raman in a qualitative way for a micrometre resolution [3]. EELS shows an advantage for more fundamental aspects and is able to answer some of the questions in terms of carbon re-hybridization (core loss and low loss) and dehydrogenation (residual peak) at small spatial scales [25].

**4.2.1 Core Loss.** The values measured are typical for amorphous carbon materials (around 70%) [24]. Overall, major coating structure (bulk) maintains the original range except coating following ZDDP lubricated test where the sp<sup>2</sup> content is smaller. The results indicate most of the main carbon structures remain unchanged regardless of

additives. But obviously the effect of single ZDDP additive solution has a stronger and deeper influence on the coating structure. The interface experiences a significant increase/change in  $sp^2$  content in GMO oils. Oil 5 (GMO) gives the lowest friction of all the tests. Similar trends of increases in tribological surface in Oil 2 (ZDDP) and Oil 3 (GMO+ZDDP) samples are also observed, but no big change in Oil 4 (MoDTC+ZDDP) is observed. Therefore, WDLC carbon coating surface in oil lubrication system exhibits the carbon structure change (possibly an increase in  $sp^2$  content) but such process also depends on additives used on the surfaces.

4.2.2 **Low Loss.** Although low loss spectra give a good feature in  $\pi \rightarrow \pi^*$  transition which also enables  $sp^2$  content quantification, it has been critically reviewed due to the mathematical process which requires to subtract the large zero loss peak [4]. Due to resolution limitations of the EELS module used in this study, low loss method does not seem to be an ideal way for tribochemistry studies purpose as the results have shown quite large differences. Core loss spectra have a higher resolution in this case and also involve only a larger and easier background subtraction, thus the results are more reliable and accurate.

4.2.3 **Residual.** The always appearing feature (black line in Figure 10) at ca. 287.5eV received some discussions in recent work [4, 24]. In these studies, this feature is used as an indicator/a measure of hydrogen content in the coating material ( $1s \rightarrow C-H^*$ ) [4, 24]. Oil 5 (GMO) and Oil 3 (GMO+ZDDP) have significant reductions in the integral of this residual compared with original coating at their interfaces. Some of the recent work on GMO with non-hydrogenated DLC coating has evidenced this hydrogen reduction observation via molecular dynamic modeling. [9, 10, 15, 16]. Also the residual reduction in Oil 5 (GMO) does not only happen at the interface, but also on upper layers

of the coating major structure (bulk), indicating a large scale upper layer structure change by GMO modification. This has also been evidenced by its mechanical properties change measured by nanoindentation.

Furthermore, the reduction in C-H content is, in other words, dehydrogenation. Reviewing literature of the DLC coating mechanism on GMO, the bond interaction of C-OH terminates and dehydrogenation process (formation of water) would be a possible reason for this coating with low friction [10, 15, 16]. However, the interaction and super lubricity of GMO on non-doped hydrogen free DLC coatings has only the very top interface dominantly terminated by the suggested mechanism [9, 10]. The reduction in both the coating main structure and interface of WDLC coating gives some messages that more interactions (chemically or physically) are experienced due to doping tungsten carbide. Details of the interactions need to be further studied in future work.

#### 4.3 Wear mechanism of WDLC/CI lubrication and effect of lubricant additives

As is discussed in the XPS results, there is a level of oxygen integration into the tribofilm/coating structure in oil lubricated condition. Although all the model oils give rise to **oxidized tungsten**, base oil without any additives has shown the greatest formation of tungsten oxide which led to the high wear/failure of WDLC coating. Introduction of additives in the base oil clearly controlled the oxidation level of tungsten. In other words, all the additives used in this study have changed the oil chemistry which leads to the reduction formation of tungsten oxide. However, it has not direct relationship between the level of oxidation and tribological performance. **Future work should focus on the chemical composition of the tribofilms formed on WDLC surfaces and how these films are correlated to wear mechanisms.**

#### 4.4 Summary of the lubricated WDLC/CI tribo-system and roles of lubricant additives

Figure 11 shows the summary of such a lubrication system and the role of lubricant additives in the tribological performance. For coating and additive optimization, the factors should be carefully considered.

### 5. Conclusions

- ❖ A low friction (CoF=0.06) and manageable low wear tribological system in a reciprocating test rig has been achieved by GMO solution in WDLC/CI interface. The mechanisms of this performance could be the formation of a higher  $sp^2$  surface layer with reduced hydrogen content, reduced hardness and reduced modulus. Surface analysis suggests that the change in coating structure is not only happening on the very top surface, but through the upper layers (possibly chemical adsorption due to coating structure). This is different from the traditional view of DLC coatings where coating forms functional groups on the very top surface.
- ❖ Coating surface is getting smoother after the rubbing process as is seen in AFM. However, there is no direct link between topography images and frictional performance observed physically. Thus oil tribochemistry plays an important role in friction.
- ❖ The comparison of Raman and EELS core loss spectra studies has suggested that different lubricant additives do affect the upper carbon coating structure

and can be studied by EELS from the fundamental point of view, in terms of quantifying the carbon  $sp^2$  content and dehydrogenation.

- ❖ XPS study shows that introducing additives in WDLC coating tribological system is critical in wear protection where additives act as anti-oxidants and control the level of oxidation. Selected lubricant additives reduce the formation of tungsten oxides, a more brittle material, which could lead to the failure of such coating as is seen in base oil lubrication. However, control the level of oxygen on the surface is also important for friction reduction as is seen in single GMO solution.

## Acknowledgements

This project is funded by Afton Chemical Limited. Thanks should go to Oerlikon Balzers Coating UK Limited for coating support. LY would like to thank Dr C. Wang at iFS in Leeds, for discussions about Nano Indentation platform. LY would also like to thank Professor R. Brydson, Dr M. Ward and Mr J. Harrington at LEMAS for training and discussion about FIB/TEM/EELS analysis. This work is partly presented in Tribo-Lyon 2013.

## References

1. Bobzin, K., et al., Lubricated PVD CrAlN and WC/C coatings for automotive applications. *Surface and Coatings Technology*, 2009. **204**(6–7): p. 1097-1101.
2. de Barros'Bouchet, M.I., et al., Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives. *Tribology International*, 2005. **38**(3): p. 257-264.



3. Ferrari, A.C. and J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*, 2000. **61**(20): p. 14095-14107.
4. Zhang, Z.-l., et al., Investigating the structure of non-graphitising carbons using electron energy loss spectroscopy in the transmission electron microscope. *Carbon*, 2011. **49**(15): p. 5049-5063.
5. Neuville, S. and A. Matthews, A perspective on the optimisation of hard carbon and related coatings for engineering applications. *Thin Solid Films*, 2007. **515**(17): p. 6619-6653.
6. Gangopadhyay, A., et al., Friction, Wear, and Surface Film Formation Characteristics of Diamond-Like Carbon Thin Coating in Valvetrain Application. *Tribology Transactions*, 2010. **54**(1): p. 104-114.
7. Vengudusamy, B., et al., Tribological properties of tribofilms formed from ZDDP in DLC/DLC and DLC/steel contacts. *Tribology International*, 2011. **44**(2): p. 165-174.
8. Sugimoto, I., F. Honda, and K. Inoue, Analysis of wear behavior and graphitization of hydrogenated DLC under boundary lubricant with MoDTC. *Wear*, 2013. **305**(1–2): p. 124-128.
9. Bouchet, M.I.D.B., et al., Superlubricity mechanism of diamond-like carbon with glycerol. Coupling of experimental and simulation studies. *Journal of Physics: Conference Series*, 2007. **89**(1): p. 012003.
10. Martin, J.-M., et al., Gas-Phase Lubrication of ta-C by Glycerol and Hydrogen Peroxide. Experimental and Computer Modeling. *The Journal of Physical Chemistry C*, 2010. **114**(11): p. 5003-5011.
11. Vengudusamy, B., et al., Friction properties of DLC/DLC contacts in base oil. *Tribology International*, 2011. **44**(7–8): p. 922-932.
12. Liu, Y., A. Erdemir, and E.I. Meletis, An investigation of the relationship between graphitization and frictional behavior of DLC coatings. *Surface and Coatings Technology*, 1996. **86–87, Part 2**(0): p. 564-568.
13. Mosey, N.J., M.H. Müser, and T.K. Woo, Molecular Mechanisms for the Functionality of Lubricant Additives. *Science*, 2005. **307**(5715): p. 1612-1615.
14. Yang, L., et al., Friction reduction mechanisms in boundary lubricated W-doped DLC coatings. *Tribology International*, 2014. **70**(0): p. 26-33.
15. Konicek, A.R., et al., Influence of surface passivation on the friction and wear behavior of ultrananocrystalline diamond and tetrahedral amorphous carbon thin films. *Physical Review B*, 2012. **85**(15): p. 155448.
16. Hayashi, K., et al., Fate of methanol molecule sandwiched between hydrogen-terminated diamond-like carbon films by tribochemical reactions: tight-binding quantum chemical molecular dynamics study. *Faraday Discussions*, 2012. **156**(0): p. 137-146.
17. Alov, N.V., Determination of the States of Oxidation of Metals in Thin Oxide Films by X-Ray Photoelectron Spectroscopy. *Journal of Analytical Chemistry*, 2005. **60**(5): p. 431-435.
18. Aouadi, M.S., et al., Characterization of sputter deposited tungsten films for x-ray multilayers. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 1992. **10**(2): p. 273-280.
19. Moulder, J.F., et al., *Handbook of X-ray photoelectron spectroscopy*. Vol. 40. 1992: Perkin Elmer Eden Prairie, MN.

20. Moreno-Castilla, C., et al., Tungsten and Tungsten Carbide Supported on *Activated Carbon: Surface Structures and Performance for Ethylene Hydrogenation*. *Langmuir*, 2001. **17**(5): p. 1752-1756.
21. Polcar, T., et al., Complex frictional analysis of self-lubricant W-S-C/Cr coating. *Faraday Discussions*, 2012. **156**(0): p. 383-401.
22. Molina-Sánchez, A. and L. Wirtz, Phonons in single-layer and few-layer MoS<sub>2</sub> and WS<sub>2</sub>. *Physical Review B*, 2011. **84**(15): p. 155413.
23. Viršek, M., et al., Raman scattering of the MoS<sub>2</sub> and WS<sub>2</sub> single nanotubes. *Surface Science*, 2007. **601**(13): p. 2868-2872.
24. Daniels, H., et al., Investigating carbonization and graphitization using electron energy loss spectroscopy (EELS) in the transmission electron microscope (TEM). *Philosophical Magazine*, 2007. **87**(27): p. 4073-4092.
25. Egerton, R., *Electron Energy-Loss Spectroscopy in the Electron Microscope*. 2011: Springer.

## Figure Captions

Fig. 1. Structure of WDLC coating by a TEM cross-section study

Fig. 2. Loading and unloading curve from one complete indentation cycle of the WDLC coating

Fig. 3. Friction and wear of the tribological tests

Fig. 4. AFM topography images showing the effect of additives on the different types of wear

Fig. 5. SEM image of wear on WDLC coating lubricated in base oil

Fig. 6. Effect of additives on the change of mechanical properties of the upper carbon coating layers

Fig. 7. XPS study on the chemical states of tungsten doped in DLC coating worn regions

Fig. 8. Effect of additives on the correlation between carbon structure and friction

Fig. 9. EELS carbon low loss spectrum of the original WDLC coating

Fig. 10. Carbon K-edge EELS core loss spectrum of the original WDLC coating

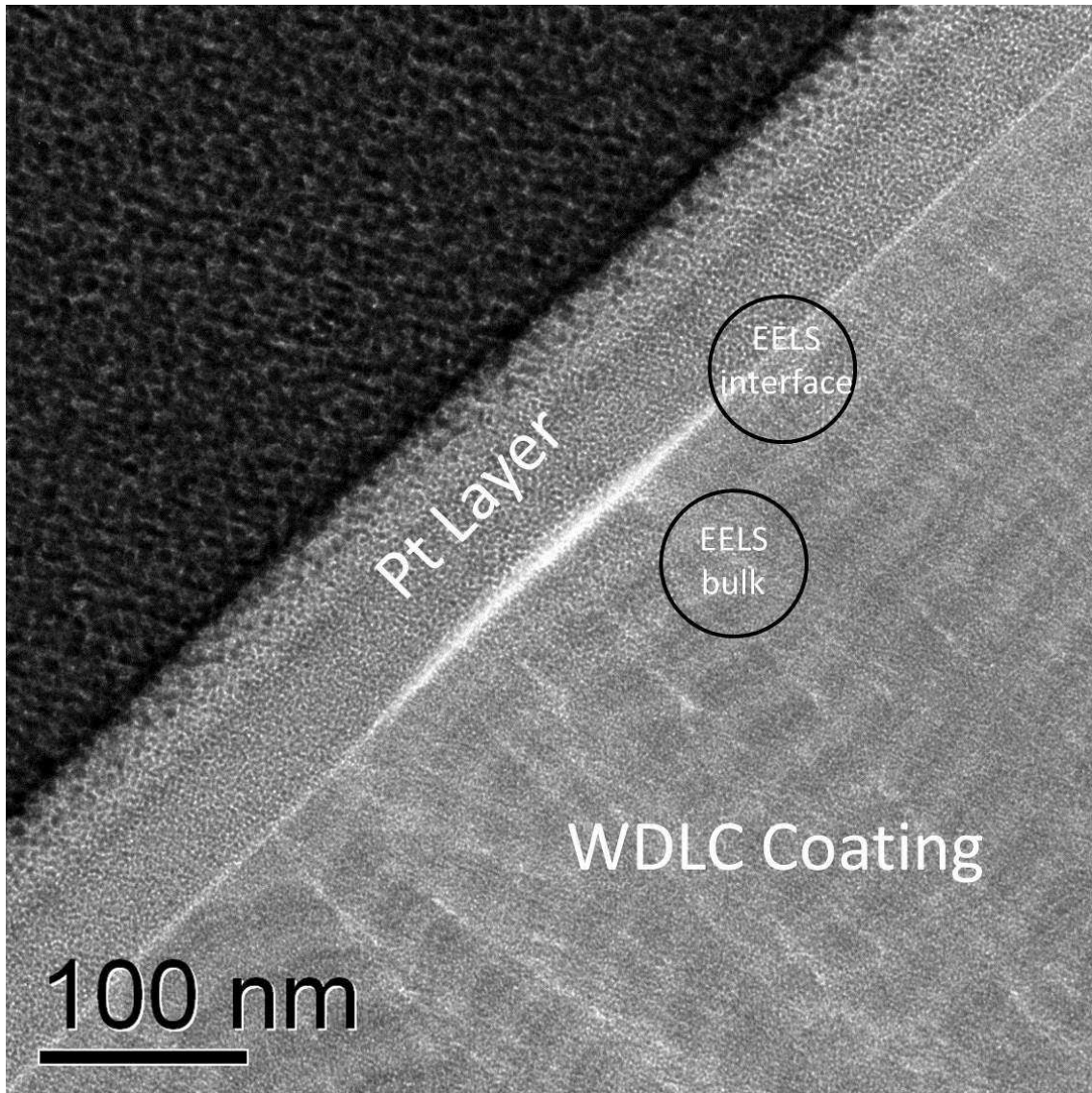
Fig. 11. Summary of WDLC/CI lubrication system and the role of additives

## **Table Captions**

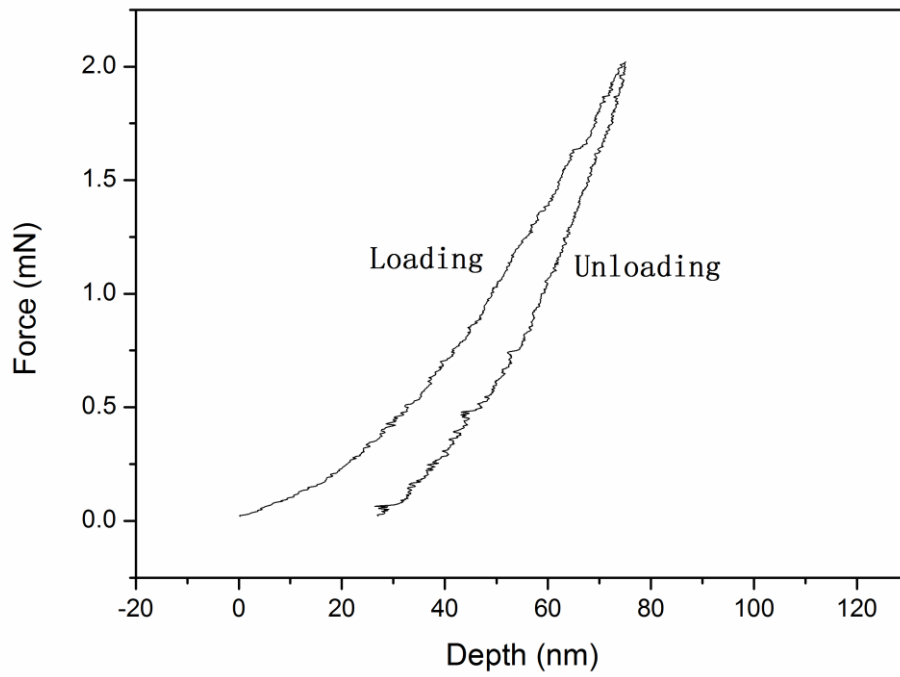
Table 1 WDLC original Coating Characterization.

Table 2 Model lubricants used in the reciprocating tests.

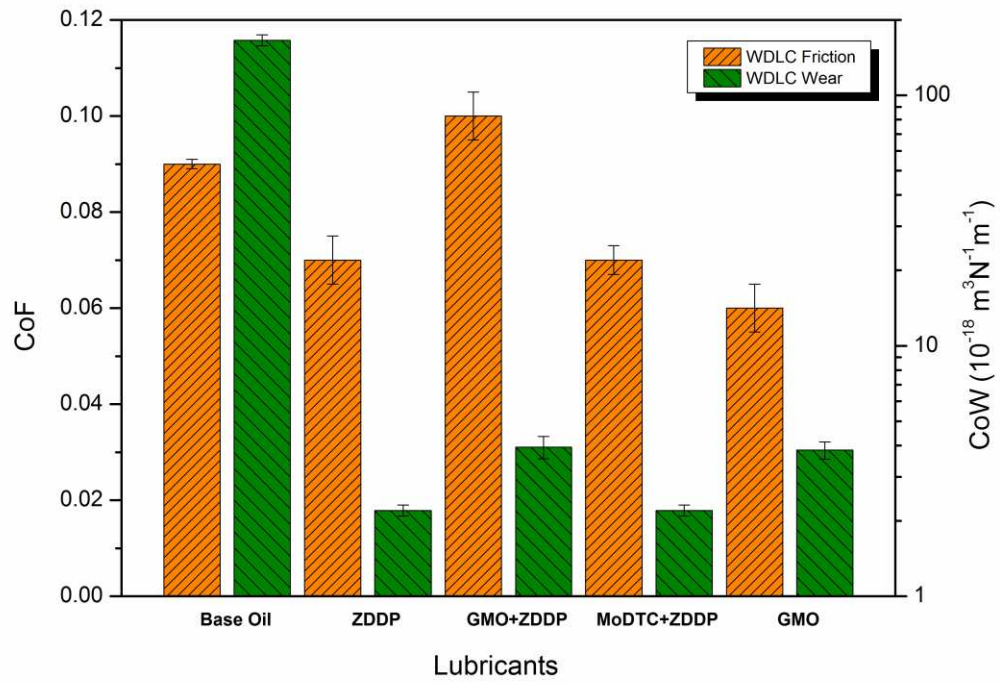
Table 3 EELS quantification of carbon  $sp^2$  content of the post tribo-test worn regions



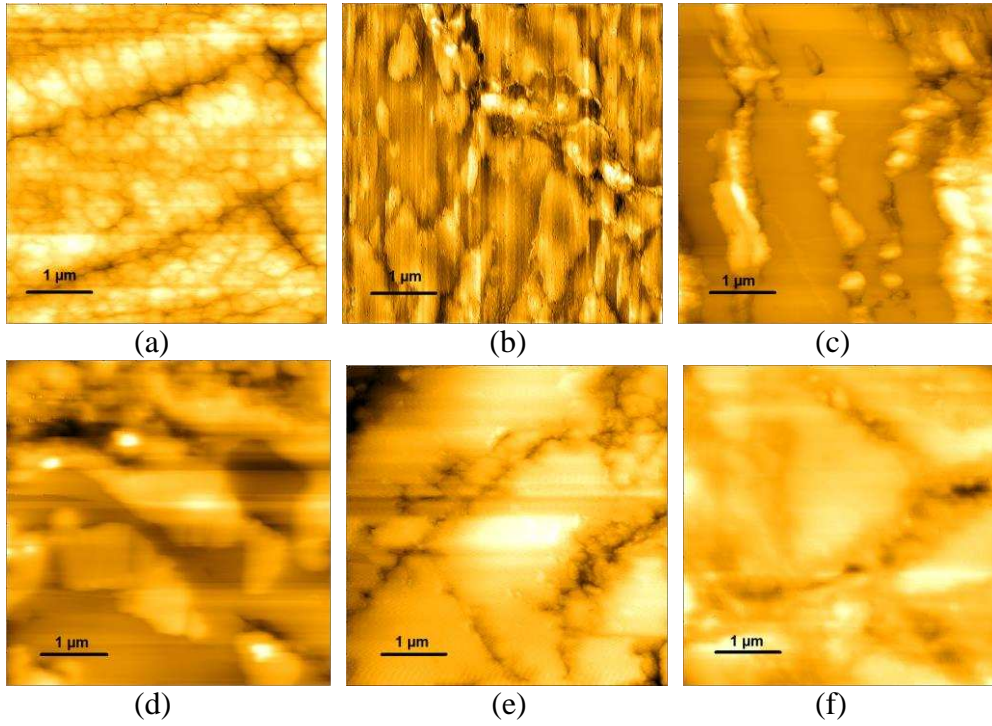
**Fig. 1.** Structure of WDLC coating by a TEM cross-section study



**Fig. 2.** Loading and unloading curve from one complete indentation cycle of the WDLC coating

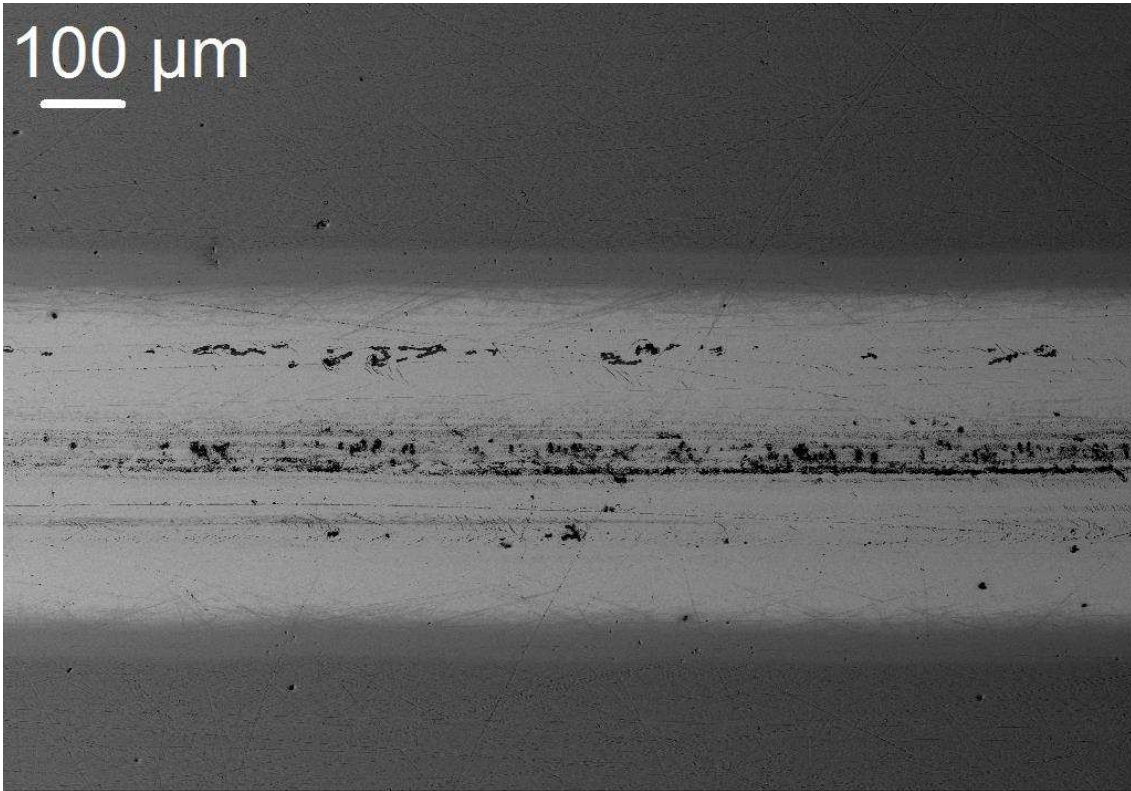


**Fig. 3.** Friction and wear of the tribological tests

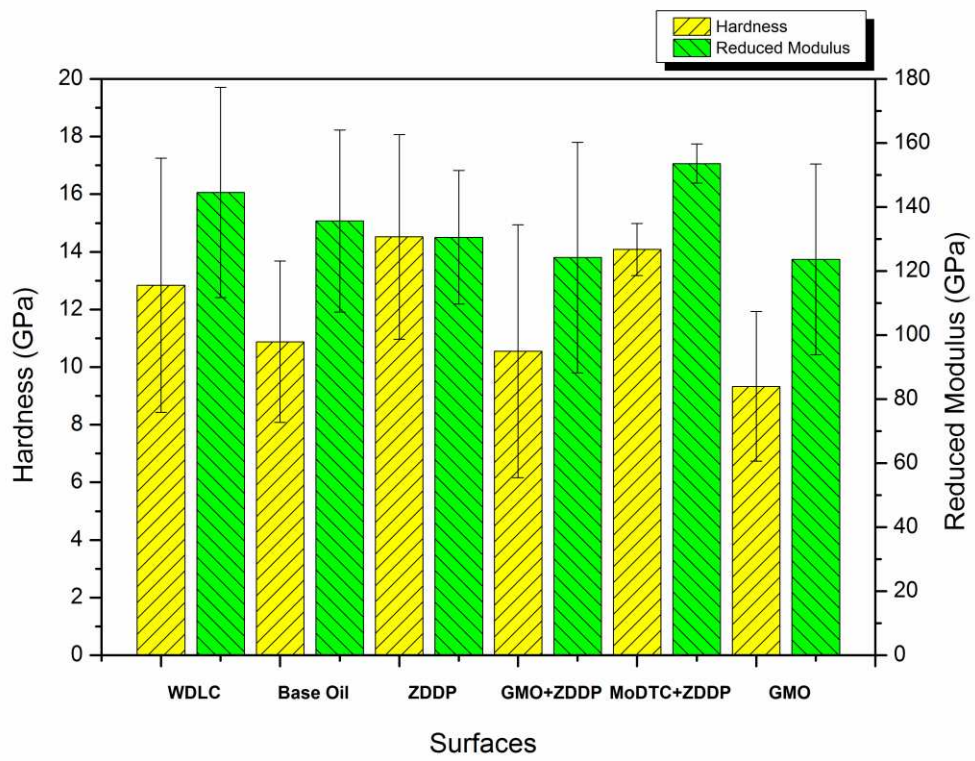


**Fig. 4.** AFM topography images showing the effect of additives on the different types of wear (a) WDLC coating; (b) Base oil; (c) ZDDP; (d) GMO+ZDDP; (e) MoDTC+ZDDP; (f) GMO

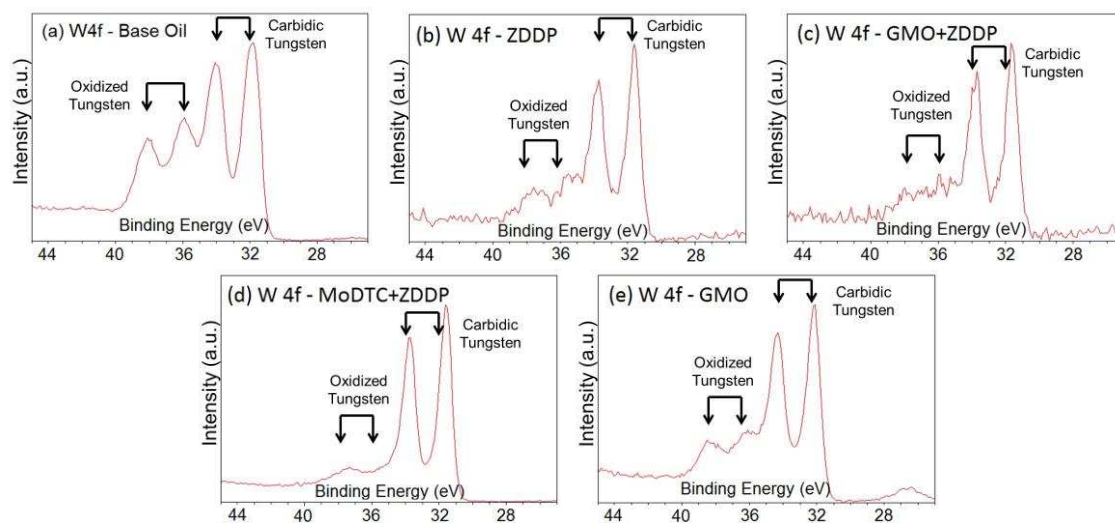




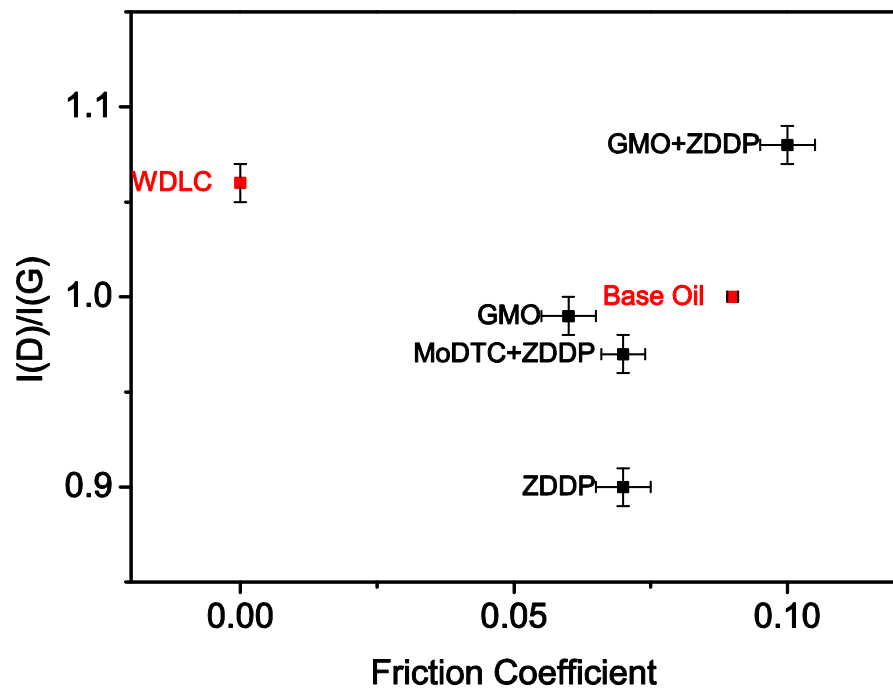
**Fig. 5.** SEM image of wear on WDLC coating lubricated in base oil



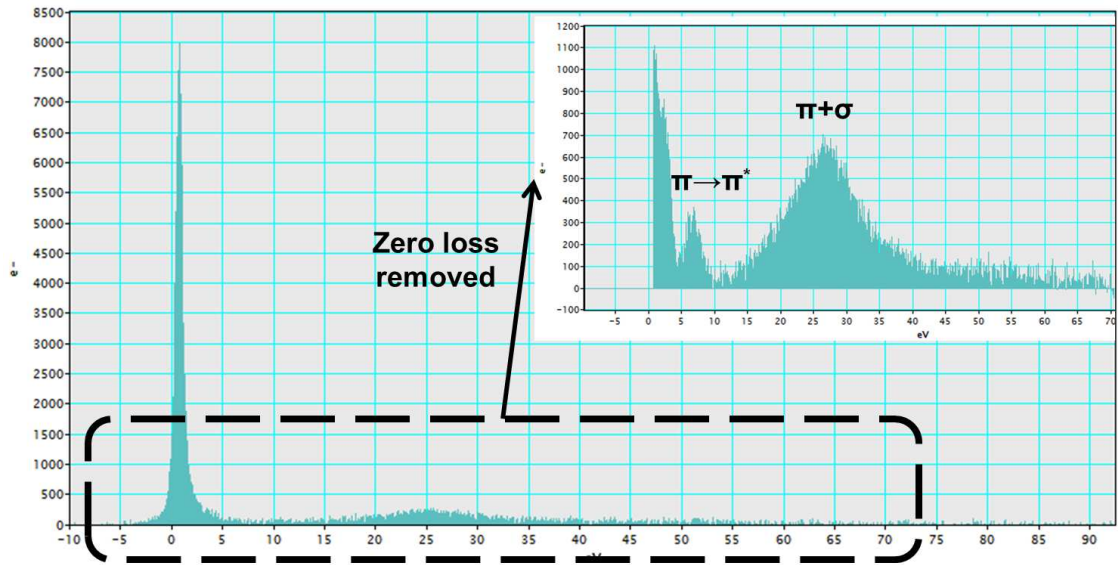
**Fig. 6.** Effect of additives on the change of mechanical properties of the upper carbon coating layers



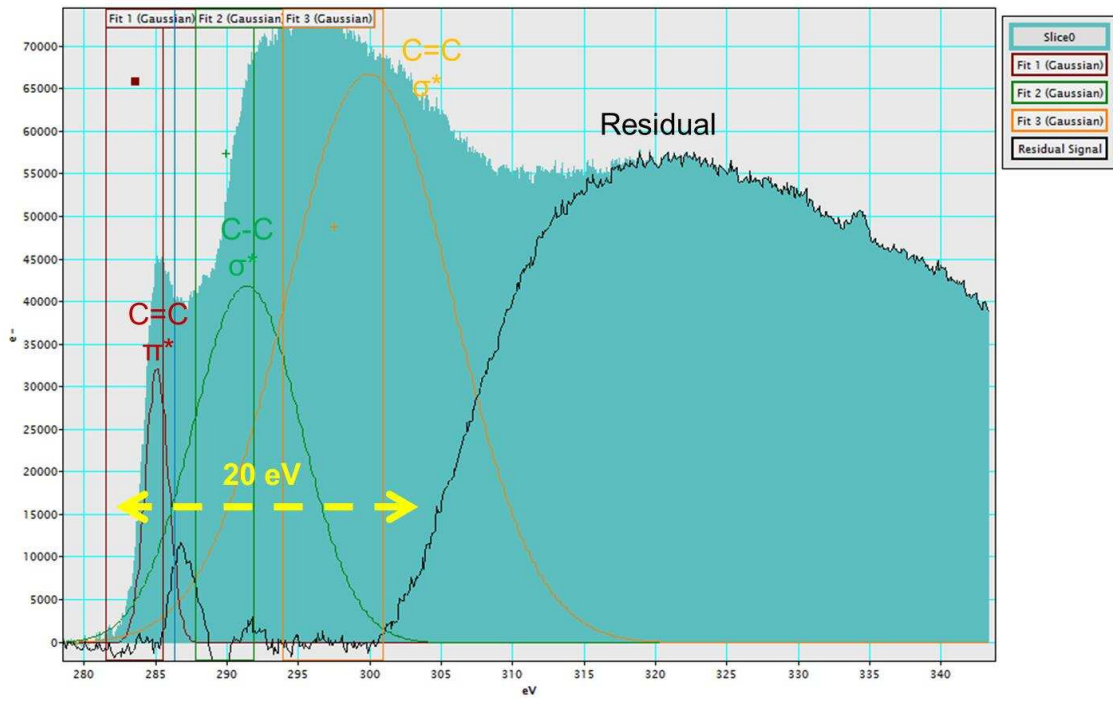
**Fig. 7.** XPS study on the chemical states of tungsten doped in DLC coating worn regions (a) W4f-Base oil; (b) W4f-ZDDP; (c) W4f-GMO+ZDDP; (d) W4f-MoDTC+ZDDP; (e) W4f-GMO.



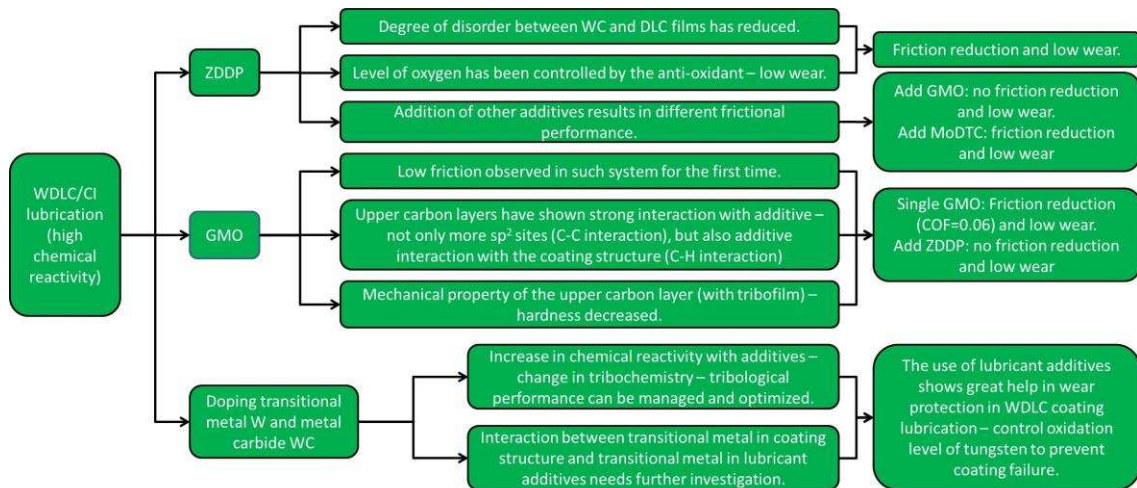
**Fig. 8.** Effect of additives on the correlation between carbon structure and friction



**Fig. 9.** EELS carbon low loss spectrum of the original WDLC coating



**Fig.10.** Carbon K-edge EELS core loss spectrum of the original WDLC coating



**Fig.11.** Summary the WDLc/CI lubrication system and the role of additives

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

Parameter	W-DLC coating	Cast iron
Raw Material Standards	AISI52100(Substrate)	BS1452
Coating/Material Hardness	12.8±4.4 GPa	4.6±0.5 GPa
Interlayers Thickness	~ 0.8 μm	-
DLC Coating Thickness	~ 2.5 μm	-
Coating Reduced Young's Modulus	145±33 GPa	148±24 GPa
Coating Roughness, R <sub>q</sub>	0.05 μm	0.1μm

\* Commercially available from Oerlikon Balzers, BALINIT<sup>®</sup> C.



**Table 2**

Model lubricants in the reciprocating tests.

Oil	Additive Type	Treat rate
Oil 1	Base oil	Poly Alpha Olefin, Group IV (PAO 4)
Oil 2	ZDDP	0.08% P
Oil 3	GMO+ZDDP	0.5% + 0.08% P
Oil 4	MoDTC+ZDDP	100 ppm Mo + 0.08% P
Oil 5	GMO	0.5%

**Table 3**EELS quantification of carbon sp<sup>2</sup> content of the post tribo-test worn regions.

Sample	Core Loss (sp <sup>2</sup> % normalized)		Low Loss (sp <sup>2</sup> % normalized)		Residual Core loss fitting (C-H* content normalized %)	
	Interface	Bulk	Interface	Bulk	Interface	Bulk
WDLC Original	77.4	77.4	66.0	66.0	28.4	28.4
ZDDP	81.3	62.6	79.2	76.1	25.8	34.0
GMO+ZDDP	80.2	75.7	54.6	77.3	23.5	32.1
MoDTC+ZDDP	77.0	77.7	78.7	75.4	33.5	30.1
GMO	90.2	72.5	67.6	67.3	14.9	15.7