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Friction and its importance in fuel economy—probing the nanoscale characteristics of surfaces in order to understand lubricant/surface interactions

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Abstract
In boundary lubrication, the critical aspect of lubrication is the interaction between the surfaces making up the tribocouple and the lubricant additives, yielding what is commonly known as the tribofilm. This has been widely studied in ferrous systems and the complex nature of the tribofilms, in terms of their self-healing, smart and semi-solid properties, is generally well understood. There is much emphasis by lubricant formulators and original equipment manufacturers on enhancing fuel economy of tribological systems whilst retaining good durability. To achieve this, surface engineering is often used and carbon-based coatings such as diamond-like carbon (DLC) are increasingly applied. Understanding the tribochemistry of such coatings against ferrous surfaces is not trivial, and this paper illustrates the contrast in features of tribology/tribochemistry behaviour between ferrous and a-C (non-hydrogenated) DLC coating. Whilst there is a clear link between low friction tribofilm composition (in terms of MoS_2/MoO_3 ratio) and friction performance for ferrous systems it is more complex for the a-C coating system; therefore an understanding of the interface microscale/nanoscale chemical and physical structure gives an insight into the interactions between friction and wear processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Tribochemistry is a subject that brings together the disciplines of tribology, chemistry, physics, surface science and surface engineering to understand reaction processes occurring at lubricated contacts. Since the word 'Tribology' became popular in the 1960s tribochemistry has always been an important area which has received extensive coverage by researchers across the globe. However, several key changes in the lubrication landscape have meant that in the last decade tribochemistry has assumed a greater importance. These include the changes in legislation relating to the use of S and P in lubricants which has meant that formulations have had to progressively become more 'green' and the increased demand for higher fuel economy from passenger and commercial vehicles which has meant a move to lower viscosity oils. Lower viscosity oils, in parallel with the increasing trend for engine downsizing, leads to more direct contact between surfaces and the tribochemical processes assume increased importance.

In referring to the Stribeck diagram (figure 1) which has been presented in many forms by researchers across the decades [1–3] the key regions are the mixed and boundary lubrication regimes. As the film thickness ratio (λ) decreases beneath around 3 the lubrication regime is classified as the mixed regime and here the liquid lubrication film separating the surfaces is discontinuous and so there is intermittent asperity contact. At $\lambda < 1$, which is referred to as the boundary lubrication regime, the lubricant film separating the surfaces no longer exists and the performance of the interface is dominated by a reaction film, the tribofilm, which is formed as a result of interactions (chemical and physical) between the

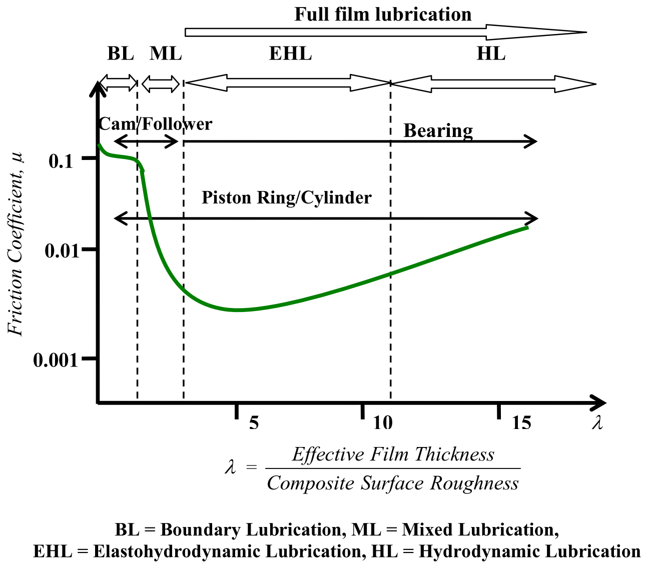


Figure 1. Stribeck diagram as presented in [1] to show the key lubrication regimes.

Table 1. Model oils (mono and binary additive systems).

Model oils	Reference
Base oil (PAO6) + ZDDP	ZDDP
Base oil + moly dimer	MD
Base oil + moly dimer + ZDDP	MD + ZDDP
Base oil + moly trimer	MT
Base oil + moly trimer + ZDDP	MT + ZDDP
Additive concentrations in oils:	
1.12 wt% moly dimer	
1.0 wt% moly trimer (Mo concentration in both	
Moly additives is 500 ppm)	
0.64 wt% ZDDP (P concentration is 500 ppm)	

lubricant and the near surface regions of the tribocouple. The Stribeck diagram does not represent the true picture in relation to performance of lubricated contacts where the lubricants contain functional additives to modify friction, protect against wear, prevent oxidation, provide dispersency etc. Surface active lubricant additives can significantly affect the nature of the tribofilm and thus affect the friction performance in the boundary and mixed regimes.

Representing the friction coefficient across the boundary lubrication regime as a relatively constant value until seizure does not properly represent the system and in reality the friction coefficient can, by design, be made to reach values of <0.05 through modification of the lubricant formulation [4–7]. Achieving this while maintaining good durability is one challenge faced by formulators and this becomes tougher as the allowable chemistries which can be used in engine oils becomes restricted. The Stribeck diagram also does not consider the chemical nature of the tribocouple surfaces and across the hydrodynamic lubrication regime of course this assumes little importance. However, as mixed and boundary lubrication regimes are reached, as stated previously, the nature of the interface is paramount and so the absolute values of friction across these regimes can be affected by surface engineering.

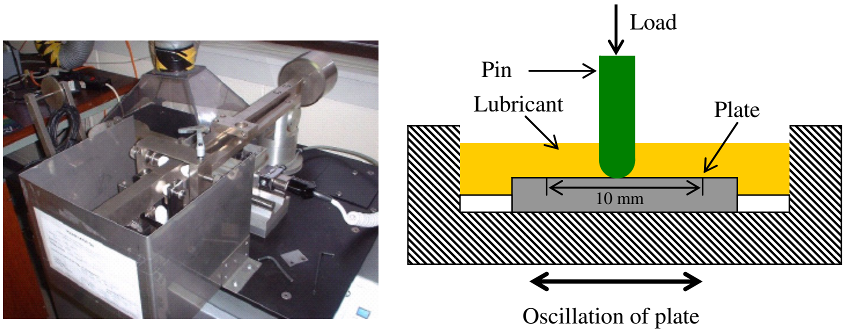
All current engine friction mathematical models struggle to accurately predict the friction performance in the mixed and boundary regimes [8]. This is primarily because of the complexity of the processes involved at the interfaces. It is currently not possible to find a universal relationship between lubricant formulation, tribocouple and the friction behaviour—some empirical models are being developed [9] but having a model which deals with the dynamicism of the problems and the kinetics of the interfacial chemical and physical reactions is still some way off. Progress is currently focused towards understanding the links between the macroscopic tribocouple performance, which is often recorded in terms of friction and wear, and the micro/nanoscopic characteristics of the resulting interface. This paper addresses this for two material systems chosen to represent a conventional material system (uncoated steel against cast iron) and a higher value material system (non-hydrogenated DLC coating) which was used initially in motorsport applications but which is being rolled out into the passenger car market.

2. Materials and methods

The chemical compositions of the model oils are listed in table 1. Two friction modifiers were used; namely molybdenum dithiocarbamate dimer (moly dimer) and molybdenum dithiocarbamate trimer (moly trimer) while the zinc dialkyl dithiocarbamate (ZDDP) (85% secondary and 15% primary ZDDP) was used as the only antiwear additive in the mono/binary oils. The poly-alpha-olefin Group IV base stock was used in this study. The dynamic viscosity and viscosity-pressure coefficient of those oils at 100 °C were 4.03×10^{-3} Pa s and α_p is 1.1×10^{-8} Pa^{-1} respectively.

Uncoated AISI 52100 steel and BS 1452 cast iron were used as the plate and pin respectively in the conventional tribocouple (referred to as UC steel/CI). The non-hydrogenated diamond-like carbon (referred to as a-C) coating was deposited onto an adhesion-promoting Cr layer which was first deposited by DC magnetron sputtering. The Cr layer was followed by a deposition of a CrC intermediate layer by the addition of hydrocarbon (e.g. butane) into the chamber. Finally, the a-C layer was deposited using a pulsed DC bias on the substrate and a discharge enhancing electrode with a 13.56 MHz RF generator. The substrate temperature was maintained less than 250 °C.

The first step of this study is to produce tribofilms using the pin-on-reciprocating plate test rig as given in figure 2(a). The contact conditions and lubrication regime used in the tests performed in this rig can simulate the most severe conditions that prevail at the cam/follower contact in the valve train of the internal combustion engine. The pin-on-plate test rig is equipped with a bi-directional load cell of the range of 58.8 N with a combined error of -0.0037 N. The combined error is defined as the combination of non-linearity, temperature effect, load cell sensitivity and hysteresis. The load cell is used to measure the friction force and the data collected from the load cell is converted to digital signal in an analogue to digital converter and finally processed by the system software. The



(a) (b)

Figure 2. (a) Biceri pin-on-plate test rig. (b) Schematic diagram of the contact in the pin-on-plate tests where the contact is submerged in lubricant.

final output comes as friction force and the readings of the friction force are taken at every 10 min for 2 s, i.e. 120 points. All data collected in the specified time gives the friction force for one complete cycle or two strokes. The average of the friction force is divided by the normal load applied on the plate which gives the friction coefficient.

The pins used in this rig were 20 mm in length, diameter 6 mm and the ends of the pins were machined with a 40 mm radius of curvature. The geometry of the flat plate was $15 \times 6 \times 3$ mm^3. The test stroke was 10 mm and the contact between the plate and pin was pure sliding in a lubricated condition as shown in figure 2(b). The sliding motion is given in the plate holding base and the lubricant is collected in the small bath. The speed is controlled by a built-in speed controller while the lubricants are heated using a heater which can maintain the set temperature using the feedback controller where a thermocouple is used to sense the temperature of the reservoir. The Hertzian contact pressure and lambda ratio were calculated.

Before starting tests, samples were cleaned using acetone in an ultrasonic bath for 15 min. The contact point of the plate and pin was submerged under a static volume of lubricant (∼3 ml) at 100 °C and the average speed was 0.015 m s^{-1}. The load was used such that the initial Hertzian contact pressure was between 600 and 700 MPa, resembling the pressure range of cam/follower contact in a passenger gasoline engine. Taking into account load, material and lubricant properties the calculated Lambda ratios were below 0.004 meaning that lubrication occurred in the boundary lubrication regime. The tests were repeated at least four times and average repeatability within 0.005 for the friction coefficient in the last hour of the test was recorded. Tests were repeated not only to check the repeatability but also to prepare samples for the purpose of various surface analyses.

X-ray photoelectron spectroscopy (XPS) was used to chemically analyse the tribofilms to a depth of a few nanometres. Although the x-ray in XPS penetrates to a depth of several micrometres, the ejected photoelectrons generally come from the depth of several nanometres from the surface. In this study, the XPS equipment of model VG ESCALAB 250 was integrated by high power monochromatized x-ray of Al Kα ($h\upsilon = 1486.68$ eV) source, high transmission electron optics, and multichannel detector. In addition to the surface analysis, this machine also provided ion etching facilities which was used for tribofilm cleaning and depth profiling purposes. Prior to XPS analysis, the excess lubricant was drained from the surface and then the surface was immersed in heptane for about 2 s, in order to eliminate the residual lubricant. The x-ray beam focused in the wear scar of the area of 500 μm by 500 μm. The pass energy for the survey scan and long scan were 150 eV and 20 eV respectively. Since the lens used in the equipment was electromagnetic, the slit width was not the concern. The argon etching was performed using Ar ions of 3 kV in the area of 3 mm by 3 mm.

The XPS survey scans were used to identify the elements present in the tribofilms and the long scans of the selected peaks were used to determine the chemical state of the compounds present in the tribofilms. Licenced CasaXPS software version 2.1.25 was used for fitting the curves on the peaks obtained from the XPS scans. Peak area ratio, difference between binding energies of the doublets and full width half maximum (FWHM) were constrained in order to obtain information with the most appropriate chemical meaning. The binding energies of the fitted peaks were compared with the values given in literature as well as various databases [10–12] to determine the compound present in the tribofilms.

The morphological/topographical features of the tribofilms were characterized using atomic force microscope (AFM). In this study, the equipment used to perform AFM analysis was Topometrix TMX 2000 Explorer (TM Microscopes), and the software used was SPMLab NT Version 5.01. The scanner head had a maximum scan range in x, y, z direction of 100 μm × 100 μm × 8 μm, respectively. Scanning was carried out in contact mode for both AFM and LFM (lateral force microscopy) analyses using silicon nitride cantilever tips with a nominal spring constant of 0.03 N m^{-1}. A constant force equivalent to 30 nA current was employed on the tip of the cantilever beam and contact mode was used to analyse the tribofilms.

3. Results and discussion

3.1. Tribological performance indicators

For the five oils the friction versus time trends for the 6 h tests are shown for UC steel/CI and a-C/CI tribocouples in

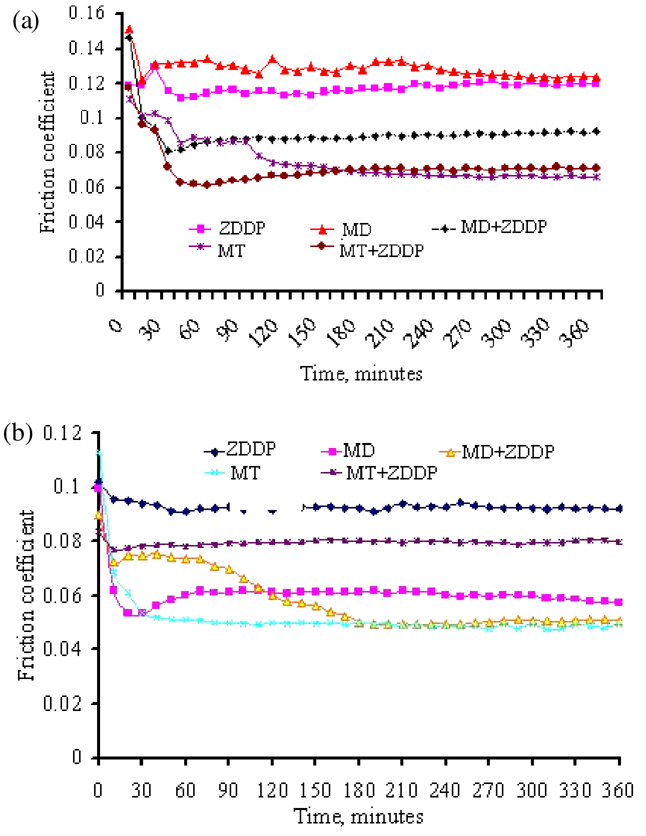


Figure 3. 3b Friction coefficient as a function of time for the (a) UC steel/CI and (b) a-C/CI systems using model oils.

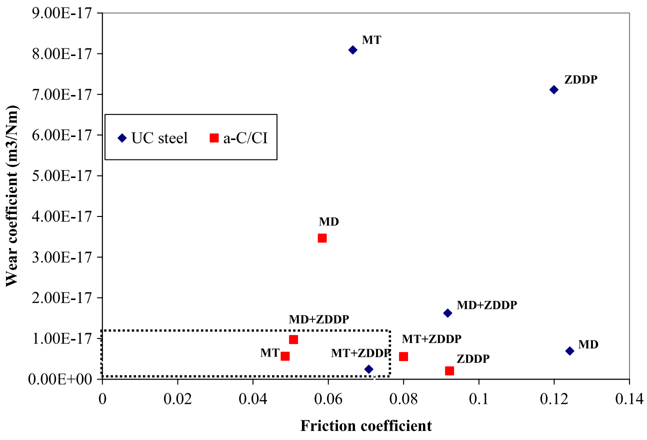


Figure 4. Wear versus friction for all tests—black box indicates optimum performance.

figures 3(a) and (b) respectively. The friction values for all oils are clearly in a steady state regime after 180 min. During that time there are mechanical and tribochemical processes occurring between surface asperities and also the wear process reaches the steady state. For the evaluation of the friction performance the 'final' friction coefficient is referred to and it is representative of the steady state value. In the case of steel lubrication, it is generally accepted that in the steady state the friction is controlled by balancing influences from tribofilm removal (by the physical action of the rubbing) and tribofilm formation (catalysed by the tribological processes) [13–15]. From the friction results the oils can be ranked in terms of their performance and from this some comparable trends are seen for the two tribocouples; MT offers low friction and ZDDP provides high friction for both. However, comparing the tribochemistry of the two couples is by no means trivial and a simple analysis of only the friction performance can be misleading. The rest of this paper is focused towards understanding the system performance (in terms of friction and wear) and then assessing what the key indicators of performance are when assessing the micro/nano scale chemical and physical features of the tribofilm interface.

Friction reduction to achieve enhanced fuel economy must be accompanied by optimum durability and so to assess system performance the two together gives a much more comprehensive picture than friction alone. Indeed low friction can be achieved by near to catastrophic wear as has been shown in a recent paper [16]. For an assessment of durability the surface is examined after the test and for the UC steel and the a-C the wear rate (or dimensional wear coefficient as it is represented here) is recorded. In addition whether the coating has remained intact is a major issue and this forms a crucial part of the initial assessment of the system. For the purposes of this paper only the wear of the plates is discussed.

Figure 4 presents the final steady state friction coefficient against the wear for the two tribocouples for the five different oils used in this study. It should be stated here that measurement of wear coefficients at these low levels can be difficult and so replication of results is required. Especially when material transfer is involved there can be uncertainties. However, in this study the results were repeatable and so this is thought to be a good representation of the wear coefficient. It is also reassuring that the thickness of the coating was not penetrated at the end of the test which agrees with the measured low wear rates plotted in figure 4. In one test using the MD oil the coating had started to delaminate as will be discussed later.

In the rest of the paper to follow an evaluation of the near surface will be presented to assist in the understanding of the link between tribological performance and key interfacial characteristics. It is therefore useful to identify the oils for the two tribocouples which provide optimum performance. These are (as shown in figure 4):

- MT + ZDDP oil for UC steel/CI
- MD + ZDDP and MT oils for a-C/CI tribocouple.

This is based on the optimum combination of low friction and low wear as highlighted in the black box in figure 4. In case of the a-C/CI tribocouple having the optimum performance obtained with an oil which does not contain ZDDP additive (MT) could be of great practical importance. ZDDP is a proven multifunctional additive but because of its harmful effect on the exhaust gas after treatment devices, its concentration is being continuously limited by the environmental legislation and eventually will be completely banned from engine oil formulations. For this reason finding an optimal solution, without use of the ZDDP additive, is very important. It should be mentioned that fully formulated oils contain a range of other

Table 2. Elemental composition in at% obtained from XPS analysis of the UC steel and a-C wear surfaces.

		C	O	N	S	P	Fe	Mo	Zn	Cr
ZDDP	**UC Steel**	52.4	20.2	-	2.6	11.9	3.2	-	7.1	2.6
	a-C	86.1	8.5	-	1.3	1.8	0	-	2.3	0
MD	**UC Steel**	36.6	32.6	14.8	2.7	-	10.6	5.7	-	0
	a-C	Coating delaminated								
MD+ZDDP	**UC Steel**	71.8	12.8	6.4	0.8	1.8	1.9	1.1	2.4	1
	a-C	78.2	5.5	12.2	0.9	0	0	2.5	0.7	0
MT	**UC Steel**	36.7	23	17.6	6.2	-	7.3	9.3	-	0
	a-C	87.5	1.1	7.4	1.4	-	0	2.7	-	0
MT+ZDDP	**UC Steel**	22	34.9	11.2	7.8	7.8	0.5	3.2	9.2	3.4
	a-C	75.1	5.2	10.3	3.8	0	0	3.6	2.3	0

additives such as detergents, dispersants, antioxidants etc and remains to be studied if the observed beneficial performance of the a-C coating lubricated with the MT model oil will be seen also when other additives are present in the oil.

The best performing oils are not common for both tribocouples—something that is not unexpected when the contrasting chemical and physical nature of the tribocouple surfaces is considered. However, understanding why this is the case is crucial for optimized lubrication of a-C/CI systems. Also, although the four oils (with the exception of MD) show very similar and low wear coefficients for a-C their friction coefficients are widely different. These features will form the rest of the discussion of the paper.

3.2. Interface analysis—tribofilm/surface characteristics

Table 2 shows the XPS quantification of the tribofilms formed on UC steel and a-C wear surfaces produced as result of the lubrication with model oils. The individual XPS spectra and the curve fitting of these peaks are given in detail in [17]. In this analysis three parameters which have been measured on the post-test surfaces are evaluated—two are chemical aspects of the near surface region (i) low friction tribofilm material and (ii) wear-reducing film glass polymerization number, and the other is (iii) the physical topography of the surface at the nanoscale as evaluated using the atomic force microscope. These will be evaluated in turn and then finally linked to the key tribological performance indicators. Table 3 is presented as a summary of all the tribological data and surface analysis results and the purpose is to evaluate the link between the two. Table 3 presents a ranking based on friction data (light grey) and wear data (dark grey) and the purpose is to show that for optimized system performance these both need to be giving good performance. On going from the top to the bottom of the table the performance improves, meaning that friction and wear are lower towards the bottom of the table. The actual values of friction and wear are given and these are used to select optimum ‘systems’. In the table the following parameters are grouped together; (i) friction coefficient and MoS_2/MoO_3 ratio (light grey) and (ii) wear, glass polymerization number (n) and topography (dark grey).

(i) *Low friction tribofilm material.* There has been much reported in the literature about the role of MoS_2 in reducing friction of tribological contacts and the nature of the MoS_2, as dispersed nanoscale sheets in the tribofilm [18, 19], has been clearly shown in recent studies. In a recent paper by the authors it was shown that there is a general connection between the MoS_2/MoO_3 ratio determined by near surface chemical analysis of tribofilms formed on steel and the friction coefficient [18]. This ratio seemed to be a better indicator of friction performance than the total amount of MoS_2 detected in the wear scar [6, 7]. In this current study it is fairly evident that at higher MoS_2/MoO_3 ratios the friction coefficient in lubricated UC steel/CI systems was reduced, levelling at 0.07 for the MoS_2/MoO_3 ratios for MT + ZDDP and MT tribofilms being 2.9 and 4.5, respectively. In this case, the tribofilm is dominated by the low friction species, MoS_2. Its performance in providing low friction is reduced when the Mo oxide concentration in the tribofilm is increased. This is understandable knowing that Mo oxide does not possess low friction properties. In the current study, formation of the MoS_2 and Mo oxides from the Moly additives has been seen for both material combinations. In work by Haque [17] it was shown that the MoS_2/MoO_3 was not the controlling factor for friction in CI/DLC tribocouples. From table 3 (b) it is clear that also for the a-C/CI couple the MoS_2/MoO_3 ratio seems to not have decisive role in determining the friction performance and are therefore other factors exerting an important influence on friction. The MoS_2/MoO_3 ratios are generally higher than for UC steel/CI (comparing tables 3 (a) and 3 (b)) but the optimum friction performance does not link to the highest MoS_2/MoO_3 value.

Kano *et al* [20] reported that the use of GMO in PAO in a-C/steel contact gave friction coefficient as low as 0.02 while

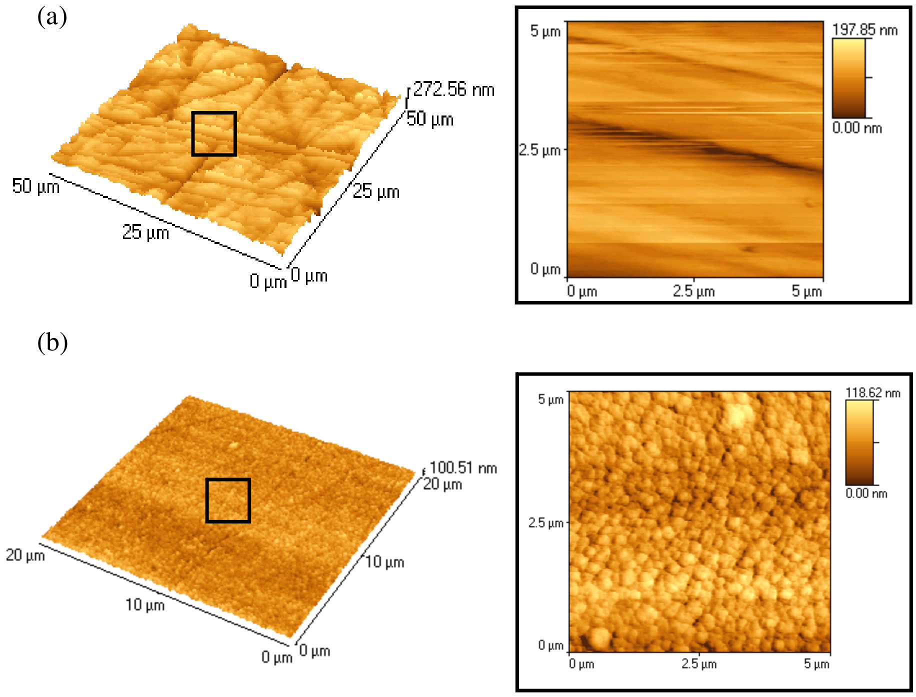


Figure 5. Atomic force microscope images of starting surface for (a) UC steel and (b) a-C coating.

Table 3. Performance ranking and surface analysis summary for (a) UC steel/CI and (b) a-C/CI systems. Friction data are presented in light grey and wear data are presented in dark grey colour. Towards bottom of the tables, performance improves while bold and underline indicates the oils which gave the best overall performance.

UC steel/CI							
Friction				Wear			
Oil	µ	MoS_2/MoO_3		Oil	Wear Coeff. (mm^3/Nm)	n	
MD	0.12	0.5		MT	8E-17	-	Micro-grooves
ZDDP	0.12	-		ZDDP	7E-17	2.7	Patchy tribofilm
MD+ZDDP	0.09	1.6		MD+ZDDP	1.6E-17	1.4	Patchy tribofilm
MT+ZDDP	0.07	2.9		MD	7E-18	-	Scoring
MT	0.07	4.5		**MT+ZDDP**	2.4E-18	2.4	Micropits and patchy tribofilm

a)

a-C/CI							
Friction				Wear			
Oil	µ	MoS_2/MoO_3		Oil	Wear (mm^3/Nm)	n	Surface characteristics
ZDDP	0.09	-		MD	3.7E-17	-	Delamination
MT+ZDDP	0.08	11.9		**MD+ZDDP**	9.7E-18	-	Smooth
MD	0.06	-		**MT**	6E-18	-	Smooth
MD+ZDDP	0.05	3.2		MT+ZDDP	5.5E-18	-	Grains/nodules
MT	0.05	6.6		ZDDP	2E-18	2	Tribofilm and grains/nodules

b)

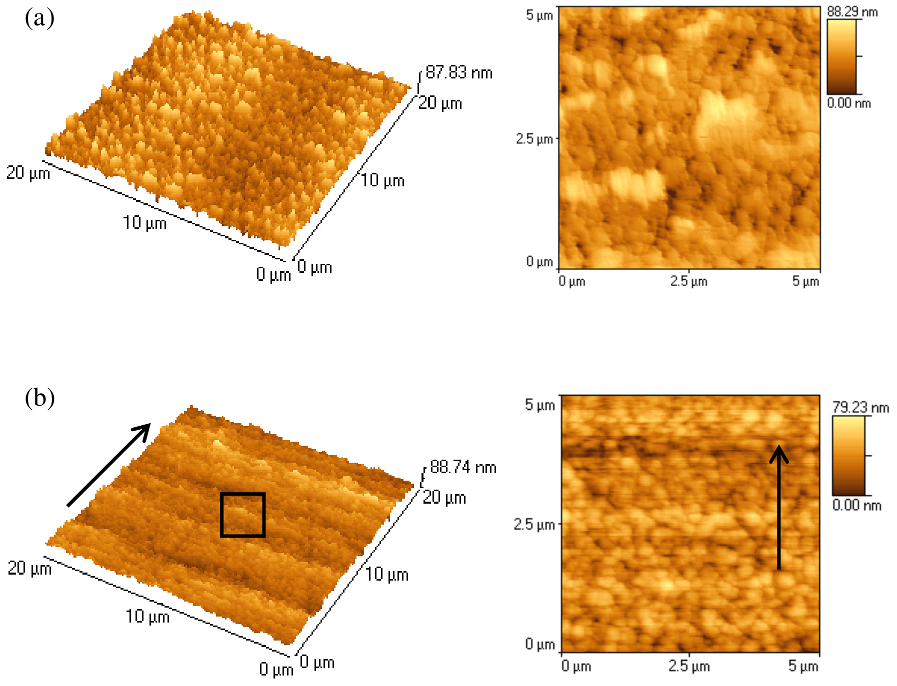


Figure 6. Atomic force microscope images of a-C surfaces associated with optimum *wear* performance—initial microstructure is retained. (a) ZDDP alone and (b) MT + ZDDP.

it was 0.08 using fully formulated oil. In the current work the DTC part of the Moly additives molecule is shown to form a film too, indicated by the presence of nitrogen peaks. The effect of this film on friction is still not clear and needs further study.

In general, the suggestion is that the friction at the interface in the lubricated a-C/CI contact is governed by factors other than the MoS_2/MoO_3 ratio. This will be further discussed when the high resolution surface topography is discussed (in iii).

(ii) *Phosphate glass polymerization number.* Before looking at the glass polymerization number, defined as the ratio of *bridging* (P–O–P) to *non-bridging*(–P=0 and P–O–Zn) oxygen, $BO/NBO = (n-1)/2(n+1)$ [21] it is important initially to look at the presence of elements, typically known to produce wear-reducing films on the steel components, on the a-C surface.

Wear scar analysis by XPS showed that in the a-C coating P was present only when the oil with ZDDP was used. Its concentration was 1.8 at.% compared to 11.9 at.% for the same oil on the UC steel surface. With the MD + ZDDP and MT + ZDDP oils no P was detected at all. In evaluating the wear performance of a-C the ZDDP oil gave the best wear performance but there was little difference between the MD + ZDDP, MT, MT + ZDDP and ZDDP oils. With the ZDDP—containing oils, whereas on the UC steel the tribofilm is dominated by phosphate glass species, on the a-C coating the main species were ZnO/ZnS—found on all tribofilms. MT + ZDDP and MD + ZDDP gave very different friction behaviour yet their Zn species on the surface were comparable suggesting these do not have a major influence on friction. It should be remembered that the counterface material is ferrous based for the a-C and there is a potential for transfer of material from the pin to the harder a-C coating. On all a-C surfaces analysed after the tests no Fe is found on the near surface of the wear scar and so macroscopic transfer from the pin to plate does not occur.

It is however feasible that there is transfer of the tribofilm from the pin to the a-C coated plate; something which seems a likely explanation for how P-containing glass comes to be detected in the ZDDP couple. From analysis of the pins the concentrations of P on the pins using ZDDP, MD + ZDDP and MT + ZDDP are 3.5, 0 and 1.1 respectively.

Linking the chemistry of the tribofilm to the wear performance of the surface is therefore not simple and a general trend of lower *n* to give lower wear is not found as is shown in table 3.

(iii) *High resolution surface topography.* The previous assessments of the wear surface region in (i) and (ii) have focused on chemical species which primarily affect friction and wear. In this section the near surface topography is assessed. The starting point to assess the tribology/tribochemistry/topography link is to compare the initial starting surface (ground in the case of US steel and as-deposited for the a-C coating). These are shown in figures 5(a) and (b).

Delamination was seen to initiate with the MD lubricant and this surface tribochemistry will not be further discussed. For the MD + ZDDP, MT, MT + ZDDP and ZDDP the topography was clearly similar for MD + ZDDP and MT and also similar for MT + ZDDP and ZDDP although only small differences in wear were recorded. Ultimately the best wear performance was associated with a nanoscopic structure which was comparable with the original surface—

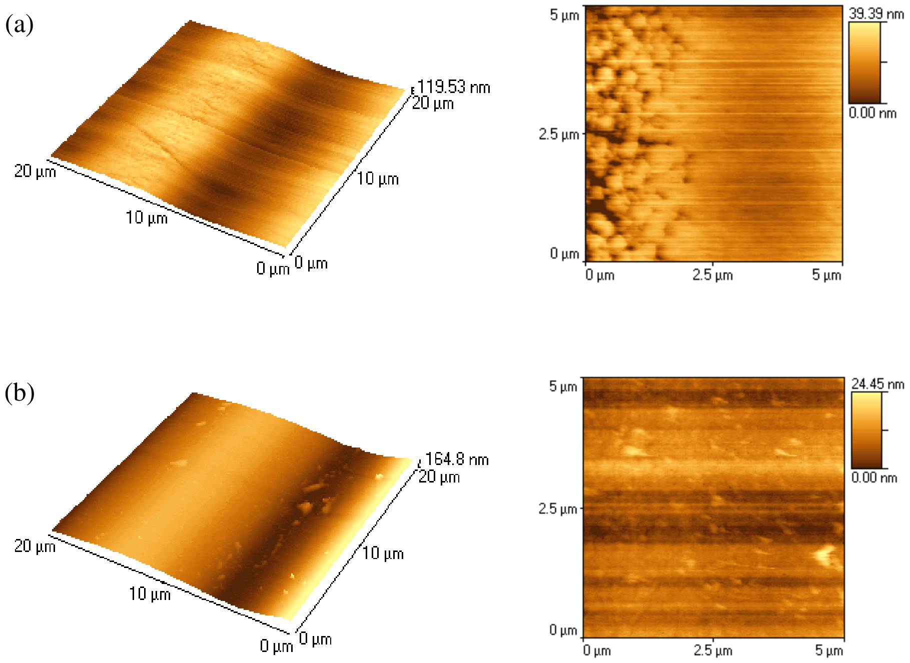


Figure 7. Atomic force microscope images of a-C surfaces associated with optimum *wear and friction* performance—small wear rate leads to a loss of the initial microstructure but leads to low friction. (a) MD + ZDDP alone and (b) MT.

i.e. the distinct nodular/grainy microstructure was retained. The surfaces for ZDDP and MT + ZDDP oils where negligible wear had occurred are shown in figures 6(a) and (b). Where an optimum combination of friction *and* wear is achieved the initial microstructure of the surface is lost and a featureless surface is observed (figures 7(a) and (b)). This is indicative of there being a strong link between the wear and friction processes; with these oils a small wear rate is associated with the production of reaction products at the interface, derived from both the a-C coating and the CI pin, and these products are instrumental in producing low (optimum) friction.

4. Concluding comments

The controlling parameters in lubrication of non-ferrous, and in particular non-hydrogenated DLC coatings (a-C) are in contrast to those influencing lubrication of ferrous systems. Tribofilm formation, occurring through a complex series of chemical reactions at the near surface under tribological contact, is central to the performance of the ferrous systems and P-containing tribofilms are known to comprise glassy constituents which provide wear protection. On ferrous systems friction is dominated by the ratio of sulfide to oxide Mo-containing compounds. In a-C surfaces, tribochemical reactions occur and this paper has demonstrated that tribofilms are formed but there is not a systematic link between tribofilm composition and performance. This is because in addition to the tribofilm composition the microstructure of the coating and the potential phase changes which occur during rubbing are key and these control the friction and wear at the interface. Challenges in optimizing lubrication for carbon coatings must therefore consider these complexities. This paper has demonstrated that there is potential for lubrication of the C-based coatings by oil formulations free from phosphorus. The integration of tribological experimentation and advanced surface science is instrumental in providing the information required to design next generation lubrication systems.

References

[1] Priest M and Taylor C M 2000 Automobile engine tribology—approaching the surface *Wear* **241** 193–203
[2] Morina A 2005 Lubricant additive interactions, surface reactions and the link to tribological performance in engines *PhD Thesis* Heriot-Watt University, Edinburgh, UK
[3] Bovington C H and Hubbard A 1989 Lubricant additive effects on valve train friction and wear *SAE 894021*
[4] Morina A, Green J H, Neville A and Priest M 2003 Surface and tribological characteristics of tribofilms formed in the boundary lubrication regime with application to internal combustion engines *Tribol. Lett.* **15** 443–52
[5] Voong M, Neville A and Castle R 2003 The compatibility of crankcase lubricant—material combinations in internal combustion engines *Tribol. Lett.* **15** 431–41
[6] Morina A, Neville A, Green J and Priest M 2006 ZDDP and MoDTC interactions and their effect on tribological performance—tribofilm characteristics and its evolution *Tribol. Lett.* **24** 243–56
[7] Morina A, Neville A, Priest M and Green J 2006 ZDDP and MoDTC interactions in boundary lubrication—the effect of temperature and ZDDP/MoDTC ratio *Tribol. Int.* **39** 1545–57
[8] Green J, Priest M, Morina A and Neville A 2003 Approaches to sensitising engine valve train friction models to lubricant formulation characteristics *Tribological Research and Design for Engineering Systems, Proc. 29th Leeds-Lyon Symposium on Tribology, Leeds, 2002* (Amsterdam: Elsevier) pp 35–44
[9] Roshan R, Priest M, Neville A, Morina A and Xia X 2007 Friction modelling of tribofilm performance in a bench tribometer *Proc. Inst. Mech. Eng.* J **222** 357–67

[10] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-Ray Photoelectron Spectroscopy* (Minnesota: Pelmir-Elmer Corporation)

[11] NIST 2007 XPS database (online). Available at http://srdata.nist.gov/xps/main_search_menu.htm (accessed 16 December 2007)

[12] Lasurface 2007 XPS, AES, UPS, ESCA database (online). Available at http://www.lasurface.com/accueil/index.php (accessed 16 December 2007)

[13] Morina A and Neville A 2007 Tribofilms—aspects of formation, stability and removal *J. Phys. D: Appl. Phys.* **40** 5476–87

[14] Morina A and Neville A 2007 Understanding the composition of tribofilms and kinetics of their formation/removal in boundary lubrication *Tribol. Int.* **40** 1696–704

[15] So H and Lin R C 1999 The combined effects of ZDDP, surface texture and hardness on the running-in of ferrous metals *Tribol. Int.* **32** 243–53

[16] Haque T, Morina A and Neville A 2007 Study of the ZDDP antiwear tribofilm formed on the DLC coating using AFM and XPS techniques *J. ASTM Int.* **4** JAI100937

[17] Haque T 2008 Tribochemistry of lubricant additives on non-ferrous coatings for reduced friction, improved durability and wear in internal combustion engines *PhD Thesis* University of Leeds

[18] Neville A, Haque T, Morina A and Voong M 2007 Compatibility between tribological surfaces and lubricant additives—how friction and wear reduction can be controlled by surface/lube synergies *Tribol. Int.* **40** 1680–95

[19] Barros M I D, Bouchet J, Raoult I, Mogne T L, Martin J M, Kasrai M and Yamada Y 2003 Friction reduction by metal sulfides in boundary lubrication studied by XPS and XANES analyses *Wear* **254** 863–70

[20] Kano M, Yasuda Y, Okamoto Y, Mabuchi Y, Hamada T, Ueno T, Ye J, Konishi S, Takeshima S, Martin J M, Barros M I D, Bouchet J and Mogne T L 2005 Ultralow friction of DLC in presence of glycerol mono-oleate (GMO) *Tribol. Lett.* **8** 245–51

[21] Martin J M, Grossiord C, Mogne T L, Bec S and Tonck A 2001 The two-layer structure of ZnDTP tribofilms part I: AES, XPS and XANES analyses *Tribol. Int.* **34** 523–30