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Investigation of Pure Sliding and Sliding/Rolling Contacts in a DLC/Cast Iron System Using MoDTC-Type Friction Modifier

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Abstract

Diamond-like carbon (DLC)/cast iron (CI) systems have been widely investigated due to their important application in engine components such as cylinders, pistons and more specifically for the cam/follower interface. The pure sliding contact of the DLC/CI system has traditionally been the focus of research; consequently less is understood about sliding/rolling contact systems. In addition, the tribological and tribochemical characteristics of the Molybdenum Dialkyl Dithiocarbamate (MoDTC) as a lubricant additive in such sliding/rolling contacts are not fully understood.

In this study, a Mini Traction Machine (MTM) was used to run the experiments using alloy steel balls coated with 15 atomic percent (at. %) hydrogenated DLC (a-C: 15H) rubbing against uncoated cast iron discs. Results showed that the sliding/rolling ratio affects friction, wear and tribochemistry in CI/DLC systems; pure sliding enhances MoDTC activation. MoDTC decomposes to form MoS_2, $FeMoO_4$ and not MoO_3. In addition, it was observed that MoS_2/$FeMoO_4$ ratio depends on test conditions and affects to the friction performance.

Keywords: Sliding/Rolling, Pure Sliding, DLC/Cast Iron, MoDTC.

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1. Introduction

Due to the importance of reducing emissions and improving fuel economy, there has already been a lot of effort by different scientists in developing new lubricants or/and alternative additives without compromising friction and wear performance of the lubricant. For example, the use of hybrid nanomaterials as nano-lubricant additives can reduce frictional power losses in automotive engines and can lead to an improvement in the efficiency of engines and fuel economy [1]. Results of a wide spectrum of nanoscale additives have been reported in the tribology literature and a review is beyond the scope of this paper. It is important to note that the optimisation of the frictional and durability of a tribological contact relies upon the understanding of the surface/lubricant interactions and with replacements to conventional steel now being common place, a major priority is to understand how some of the conventional friction modifiers (like Molybdenum Dialkyl Dithiocarbamate (MoDTC)) interact with conventional (steel) and less conventional (DLC) surfaces. The heavy elements can be harmful to catalytic convertors but if some of the friction reduction can be offered by the inherent surface properties then there is potential to optimise formulations. In conventional steel/steel contacts, MoDTC has been shown to produce Mo-S compounds which in turn provide low friction under boundary lubrication by forming MoS_2 low friction sheets on the tribological contact [2-4]. In addition, MoDTC additive was reported to produce MoO_3 compounds in the tribofilm [3, 5]. Moreover, the iron (II) molybdate ($FeMoO_4$) is being reported as a product of MoDTC decomposition [2, 4]. On the other hand, different studies have been focused to evaluate the interactions between MoDTC and ZDDP. Martin *et al.* [6] suggested a two-step reaction which occurs in the presence of MoDTC/ZDDP. The first reaction is between phosphate and iron oxide while the second reaction is between the nascent iron surface and a sulphide species. Essentially, it was found that Zinc DialkylDithioPhosphate (ZDDP) might promote MoS_2 formation from MoDTC sheets. In addition, it was reported that MoDTC is more effective when used together with ZDDP and the combination of both was reported to provide better tribological performance (i.e., less friction and wear) [7].

DLC coatings have attracted a lot of interest as a surface engineering solution for engine components by offering outstanding friction properties, high wear resistance, high electrical resistance, high corrosion resistance, high hardness and excellent running-in properties. Many researchers have evaluated the behaviour of DLC coatings under the presence of additives including MoDTC. It is generally shown that DLC coatings offer friction reduction by forming MoDTC derived MoS_2 sheets on DLC surfaces [8, 9]. The hydrogenated DLC films are considered to provide the counterbody with a carbon layer, where these layers are responsible to reduce friction on DLC surfaces [10]. However, recently, it has been reported [11-14] that DLC coatings wear faster in the presence of MoDTC when rubbed against a ferrous counterpart. Kosarieh *et al.* [13], showed that high concentration of MoDTC promoted wear of the hydrogenated DLC coating in oils without ZDDP but this wear was mitigated by the addition of ZDDP. Based on the published literature [3, 11-19], it appears that MoDTC-derived products are key to this detrimental effect and that ZDDP might hinder the MoDTC potency in giving high wear to DLC in the DLC/ferrous combinations [3]. MoDTC-induced wear of the DLC coatings was only observed when the DLC was rubbed against a ferrous counterpart [3, 14]. That was attributed to the formation of molybdenum-containing compounds in the presence of ferrous counterparts leading to oxidation and accelerated wear of the DLC coating [3].

Sliding and rolling contacts are widely presented in different mechanical components such as cams, gears and roller bearings. The combination of sliding/rolling motion can cause lubrication difficulties, high loads/applied stresses and film thickness variation. As a result, wear and plastic deformation can be observed which may lead to failure of the components. In the literature, however, most of the previous works have tended to focus mainly on pure sliding contacts, probably due to the fact that the pure sliding contacts are generally observed to be more severe than sliding/rolling contacts [20]. It should be noted that pure sliding contact, in most cases, does not necessarily simulate the actual contact in mechanical components as they mostly experience the combination of both motions (i.e. pure sliding and sliding/rolling). Thus, it is essential to investigate both the sliding and sliding/rolling contacts and to compare their tribological and tribochemical performance under mixed-boundary lubrication regimes. In general, the correlation between the sliding/rolling ratio (SRR) and the tribological/tribochemical performance was reported previously [2, 21-26]. For the friction performance, it has been generally shown that the increase of the sliding/rolling ratio (SRR) causes an increase of friction. For example, increasing sliding/rolling ratio from 100% to 200% increases boundary friction [2]. In addition, it was reported that elastohydrodynamic friction was increased when increasing sliding/rolling ratio from 10% to 50% [22]. Vengudusamy *et al.* [20] studied the friction behaviour of five gear oils at three different sliding/rolling ratios, 30%, 50% and 200%. They reported that the increase of the boundary friction was significant when SRR was 200% (i.e. pure sliding) while it was marginal between 30% and 50%.

The tribochemical reaction is typically attributed to the formation of a tribofilm layer. Tribofilms work as a third body between the interacting surfaces which in turn provide an ultralow friction and a low wear rate. The chemical composition of the tribofilms and/or tribofilm evolution are understood to vary with changing contact type (e.g. pure sliding contact + sliding/rolling contact). However, the understanding of the tribofilm formation due to changes in the tribological system, such as changing the type of contact (i.e. implying different SRR values) has not been given special attention. In the literature, the effect of sliding/rolling ratio on ZDDP tribofilm formation was previously investigated [25]. In addition, the tribofilm generation for a base oil and a fully formulated oil under the influence of sliding/rolling ratio was also examined [24]. Moreover, Khaemba *et al.* [2] studied the role of sliding/rolling ratio and surface roughness on the decomposition of MoDTC in a steel/steel system. However, in a DLC/CI system, there is still limited understanding about how sliding/rolling ratio affects tribofilm build-up when using lubricants containing MoDTC additive. With this understanding, the main aim of the work is to study and compare the tribological behaviour of two types of DLC/CI contacts (pure sliding contact + sliding/rolling contact) under mixed-boundary lubrication regimes. The second aim is to investigate the variation of tribofilm compositions in both contacts. This was achieved in a DLC/CI system lubricated in a fully formulated oil / base oil containing MoDTC.

2. Experimental procedure

The mini-traction machine (MTM) was used to produce tribofilms under mixed-boundary lubrication conditions, where a 19.05 mm diameter ball was loaded and rubbed against a 46 mm diameter disc and both were submerged in the lubricant. The samples were cleaned ultrasonically prior to the start of the test using acetone for at least 15 minutes. Further, the samples were wiped with a cotton bud soaked in isopropanol. Lastly, an airbrush with isopropanol was used to clean the samples from dust. Two types of tests were carried out in the MTM tribometer, (i) durability tests and (ii)

Stribeck curve tests. Durability tests are used to observe the stability of the DLC/CI system over a period of time under the boundary lubrication regime. Stribeck curve tests are used to evaluate the friction properties of the DLC/CI system under mixed-boundary lubrication regimes. The test conditions employed in this study were: applied load = 33.85 N, corresponding to a contact pressure of 0.75 GPa; entrainment speed = 100 mm/s; temperature = 100 °C; sliding/rolling ratio = 50% and 200%; running-in duration = 30 mins; test duration = 6 hrs. The entrainment speed with respect to the contacting surfaces was represented as $(u_b + u_d)/2$, where u_b is the speed of the ball while u_d is the speed of the disc. The sliding/rolling ratio was represented as the ratio of sliding speed $|u_b - u_d|$ to entrainment speed. However, SRR= 50% represents the sliding/rolling contact (this ratio is selected as a standard slipping ratio) while SRR = 200% represents the pure sliding contact (the ball was held stationary and the disc was allowed to rotate). The durability test was calculated at 100 mm/s during the whole test duration (6.5 hrs) which is in the boundary lubrication regime. The Stribeck curve test was obtained by measuring friction over a range of entrainment speeds ranging from low to high speeds, 5 to 2000 mm/s. Film thickness develops with increasing entrainment speed, progressing from boundary lubrication regime at low speed through to mixed lubrication regime at high speed.

In this study, the White Light Interferometer (Bruker NPFLEX) was used to characterize the wear of the DLC coated balls and Cast Iron (CI) disks. Therefore, before these analyses, in order to remove any physisorbed tribofilm formed on the wear scar, a droplet of ethylenediaminetetraacetic acid (EDTA) was used (by the method described in [27]) to remove the tribofilm from the analysed wear track. However, the droplet was removed with a cotton bud and the samples were cleaned with an airbrush filled with isopropanol. This was done to avoid any misleading wear measurements due to the transparent characteristics of the formed tribofilm [28]. Two-dimensional and three-dimensional images for the wear track were taken, and the average wear depth of different sections inside the wear track were calculated. Balls were made of alloy steel 16MnCr5 and discs were made of cast iron (CI). Balls were coated by commercial DLC coatings which contained 15 at. % hydrogen (a-C: 15H). The detailed physical properties of the DLC coating, balls and discs are given in Table 1. The lubricants used in the experiments are Group III mineral base oil and fully formulated oil, grade 5W30. All the oils were commercial and supplied by Total. Initially, several concentrations of MoDTC ranging from 0.1wt % to 0.5 wt % were blended with the lubricants used in this study. However, considering the test duration, it was found that the effect of these low concentrations on friction reduction was insignificant and therefore we could not discriminate between different oil formulations with regards to friction performance. For this reason, 1 wt% concentration of MoDTC was used in this work. With respect to lubricants containing ZDDP, the lubricant used was provided by Total with 1 wt% concentration of ZDDP. The detailed chemistry of oils cannot be shown due to confidentiality, but the key additive components of each lubricant are described in Table 2. In addition, a representative photograph of lubricant oil samples is shown in Fig.1. Lambda ratio and the film thickness were calculated using Equations (1) and (2) respectively [29].

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

$$\lambda = \frac{h_{min}}{\sigma_{rms}} = \frac{h_{min}}{\sum R_q} = \frac{h_{min}}{\sqrt{R_{q_1}^2 + R_{q_2}^2}} \tag{2}$$

Where h_{min} is the minimum film thickness, R is the reduced radius of curvature, U is the entraining surface velocity, η_0 is the dynamic viscosity of the lubricant at atmospheric pressure, α is the viscosity-pressure coefficient, W is the normal load, $E^{'}$ is the reduced Young's modulus, R_q is the Root Mean Square (RMS) roughness of the two surfaces in contact, R_{q_1} is the surface roughness of the DLC coating and the R_{q_2} is the surface roughness of the CI disc. The calculated Lambda ratio showed that the operating regime was boundary lubrication (λ = 0.1) for the durability test and mixed-boundary lubrication (ranging from λ=0.1 at low speed to λ = 1.2 at high speed) for the Stribeck curve tests. For BO and O1, however, the calculated Lambda ratio was not exceeding 0.9 at high speed implying a boundary lubrication regime throughout the Stribeck curve tests for these oils.

Table 1. Physical properties of balls, discs and DLC coating

	Balls	**Discs**	**DLC coating**
Specification	16MnCr5 Steel [a]	EN-GIL-250 Grey cast iron [a]	a-C: 15H [b]
Hardness	7.453-7.846 GPa	2.256-2.354 GPa	20-25 GPa
Roughness, R_q	0.02-0.05 µm	0.08-0.11 µm	0.02-0.05 µm
Reduced Young's modulus	207 GPa	110 GPa	160-200 GPa
Composition/coating thickness	C 0.16, Si 0.20%, Mn 1.11%, P 0.011%, S 0.026%, Ni 0.07%, Cr 0.90%, Mo 0.01%, Cu 0.14%, Sn 0.10%, Al 0.022%, N 0.0101%	C 3.34%, Si 2.40%, Mn 0.49%, P 0.081%, S 0.060%, Mg 0.001%	1.5-3 µm

[a] Balls and discs provided by PCS instruments, UK.

[b] Commercial coatings provided by Oerlikon Balzers Ltd., UK.

Table 2. Lubricant components

Annotations	Oil formulation
BO	Base oil B
O1	Base oil B + 1 wt% MoDTC
O2	Fully formulated oil B (free of ZDDP/MoDTC)
O3	Fully formulated oil B (free of MoDTC) + 1 wt% ZDDP
O4	Fully formulated oil B (free of ZDDP) + 1 wt % MoDTC
O5	Fully formulated oil B +1 wt% ZDDP + 1 wt% MoDTC

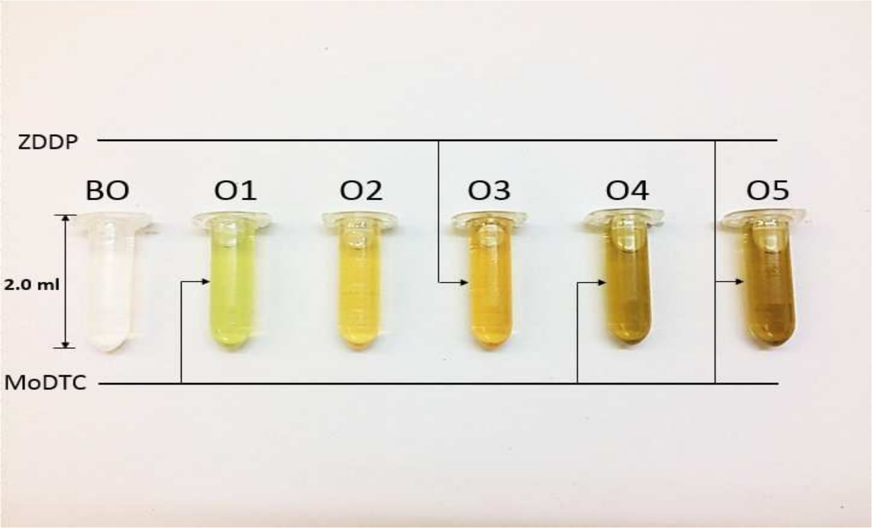

Fig. 1. Photograph showing six representative occurrence oil samples

3. Surface analysis

Scanning Electron Microscopy (SEM) was used to examine the worn ball/disk surfaces and to investigate the durability of the coatings employed. An Oxford instrumented EDX with scan size of 80 mm^2 was incorporated into the SEM device (Zeiss EVO MA15 variable pressure) to provide elemental composition of the different regions on the samples. In this work, Energy-Dispersive X-ray (EDX) spectra of the balls and the discs were obtained from inside the wear track. Raman spectroscopy has been widely used to determine the structure/composition of the tribofilms generated in a tribocontact. A Renishaw inVia^{TM} Raman spectrometer with 488 nm wavelength and 10% power filter was used to observe the structural modifications inside the wear track of the inserts. To support the results from EDX and Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) analysis was also carried out in this study. This technique allows the tribofilms chemistry to a depth of approximately 5 nm to be determined. Before using XPS analysis, all samples were cleaned using n-heptane to remove residual oil and contaminants. The electrons were excited with a micro focused monochromatic aluminium K-alpha X-ray source of 1486.6eV. A handbook of XPS was used to identify the chemical species at the respective binding energies [30]. The XPS curves were processed using the CasaXPS software. The position of the major component of the C1s peak (284.8 eV) was considered as the reference for charge correction.

4. Results

4.1. Friction results

4.1.1. The correlation between SRR and friction

Initially, the MTM durability test is essential to identify the stability of the system through a particular period. Figure 2 shows friction coefficient values during the whole test duration at 50% SRR and 200% SRR values. All MTM tests lasted for 6.5 hrs and were started with 30 minutes running-in followed by a Stribeck curve test for 1-2 minutes then a durability test for two hours. This procedure, except the running-in period, is repeated twice. The fluctuation in the data at 1800 s, 9000 s and 16200 s is where the Stribeck (speed-scanning) tests were done. In general, all oils followed the same trend with time but there were quite clear fluctuations when SRR was 200% and this resulted from the severe conditions of the test. The steady state friction, under boundary lubrication, was presented as the average friction values of the last hour of each test. Accordingly, Fig. 3 shows the average of coefficients of friction for all oils at 50% SRR and 200% SRR. It can be seen that no systematic trend of friction coefficient was observed for both SRR values. However, this is found to be due to the influence of sliding/rolling ratio on surface chemistry. Details of this will be addressed in the discussion section.

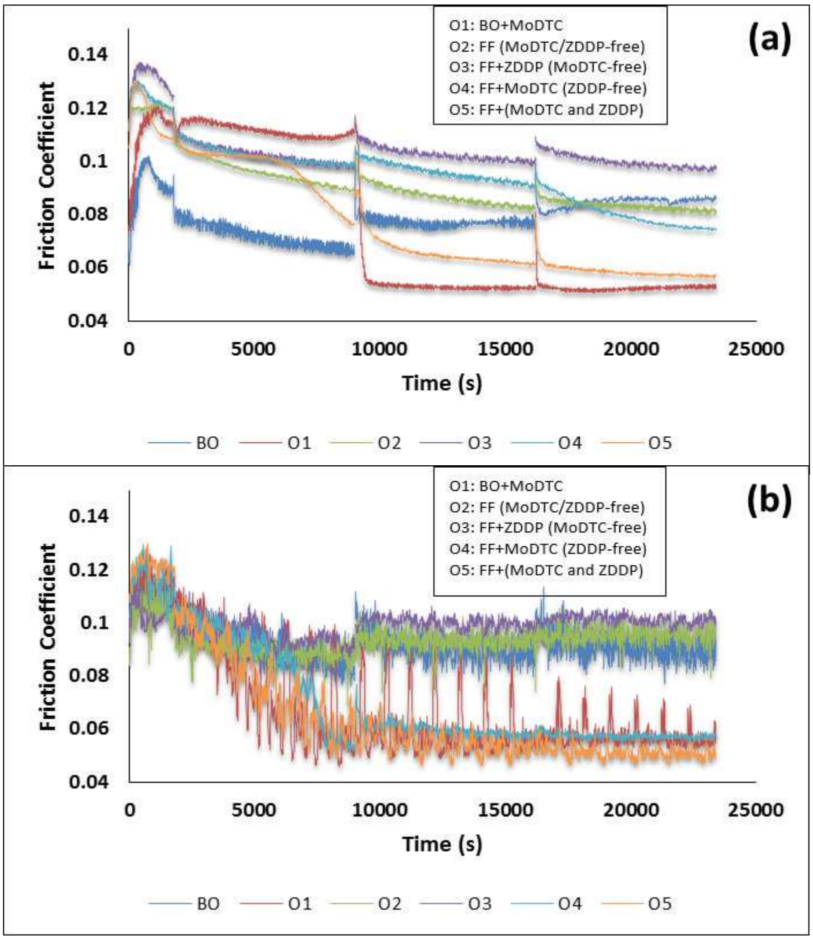

Fig. 2. Friction coefficients as a function of time: (a) at 50%SRR and (b) 200%SRR

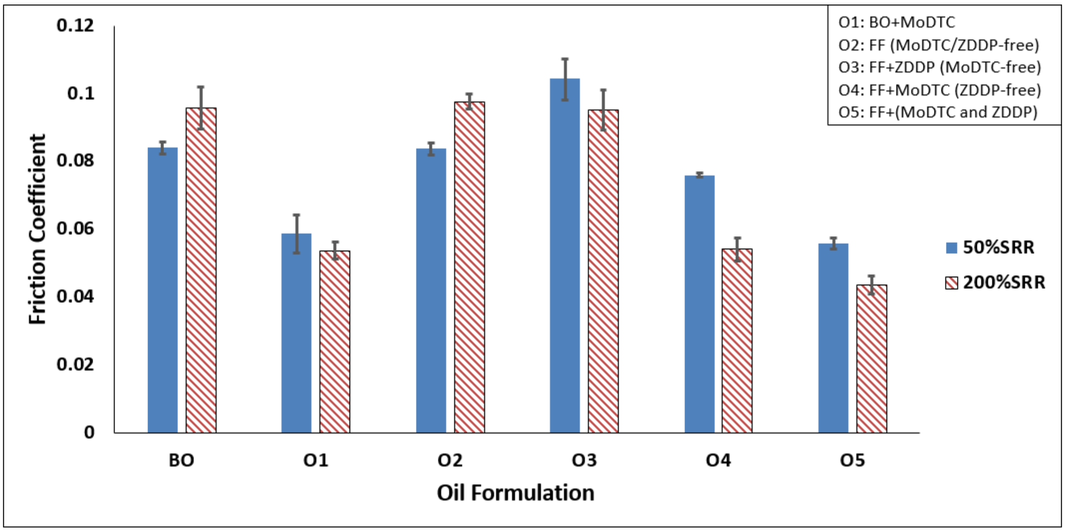

Fig. 3. Average friction coefficient values for the last hour for all oils at 50% SRR and 200% SRR

4.1.2. The correlation between SRR and Stribeck curve evaluation

The Stribeck curve evaluation gives an indication of the tribofilm build-up and the time to reach steady state conditions. Fig. 4 and 5 show Stribeck curves for each oil as a function of time and mean speed under the sliding/rolling (50% SRR) and the pure sliding (200% SRR) conditions. A systematic trend of friction coefficient was seen for both SRR values over time. For example, comparing the first 30 minutes to the following 2 hrs of the tests, friction was generally higher at 50% SRR (i.e. sliding/rolling contact) than 200% SRR (i.e. pure sliding contact) for oils containing MoDTC. This suggests a slower build-up of tribofilms in sliding/rolling contacts compared to a pure sliding contact. For the lubricants with no MoDTC (BO, O2, O3), the change in friction over time was not significant at 200% SRR. However, at 50% SRR, for O2, a considerable change in friction over time was seen suggesting tribofilm evolution over a much longer timeframe.

In order to have a better picture of the SRR effect on the tribological behaviour of the lubricants under the boundary lubrication regime, friction coefficients for each oil at mean speed = 10 mm/s represents the boundary lubrication regime were plotted (see Fig. 6) at 50% SRR and 200%. From Fig. 6, it can be seen that SRR can play an important role in the frictional behaviour for the lubricants containing MoDTC (i.e. O1, O4 and O5). In particular, pure sliding contact enhanced the activation of MoDTC over time. It is also interesting to note that the lubricant with ZDDP only (i.e. O3) was not affected by different SRR values and the friction responses were comparable over time. The observed reduction or difference in friction between both contacts was expected to be influenced by change in surface roughness over time in addition to changes in surface chemistry. The surface roughness for balls and discs at the end of each test was investigated, as shown in Table 3. Comparing the surface roughness after the test to the initial roughness (see Table 1), rougher surfaces were observed for both the discs and the balls after the tests. Nevertheless, friction reduction was reported over time for most oils. The tribological performance is more controlled by the contact type and the tribofilm formed on the ball/disc tribopair rather than the surface roughness. This means that the Lambda ratio progressively decreases as the tests progress and the lower friction is dominated by the action of the tribochemistry effect.

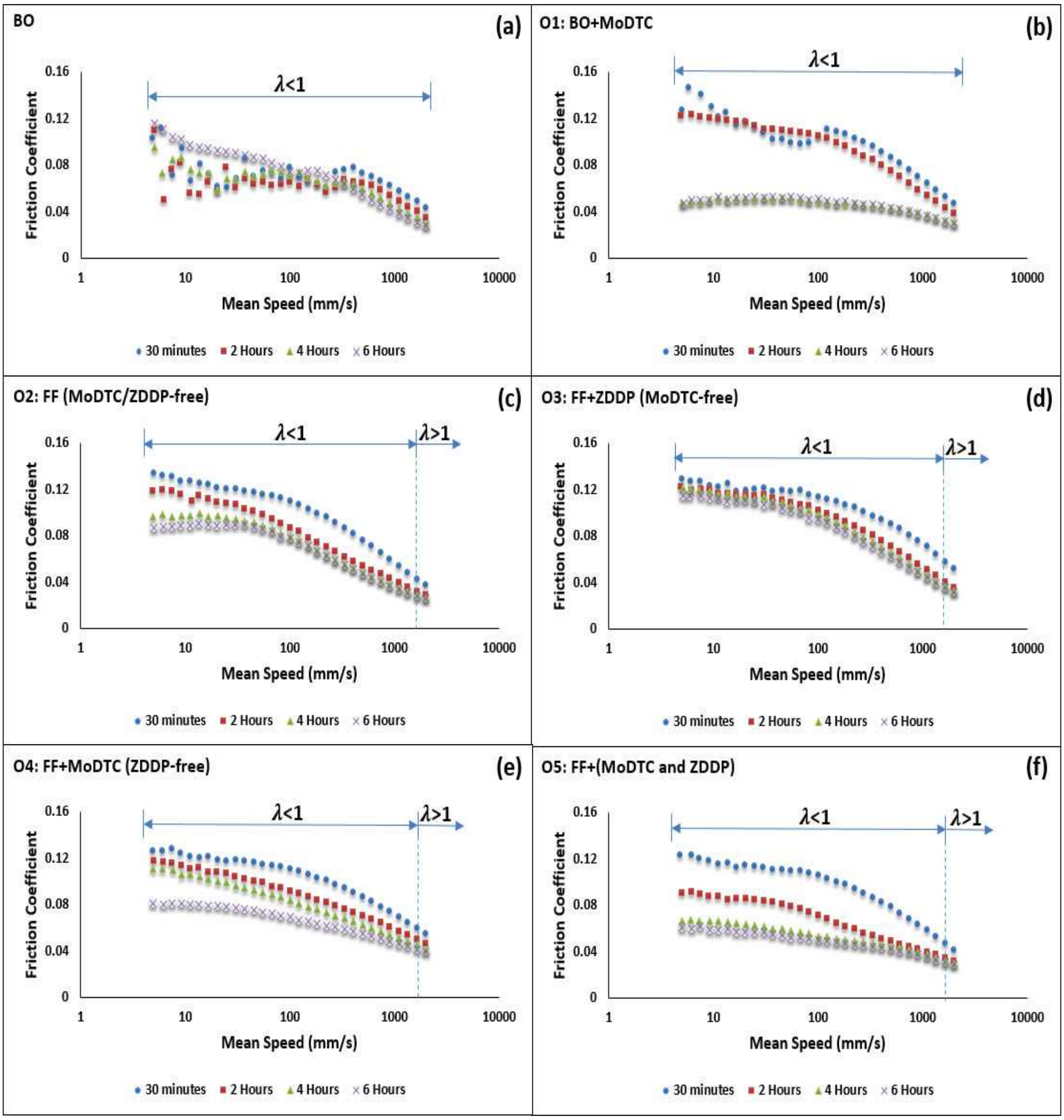

Fig. 4. Stribeck curves for (a) BO, (b) O1, (c) O2, (d) O3, (e) O4 and (f) O5 as a function of time at 50% SRR

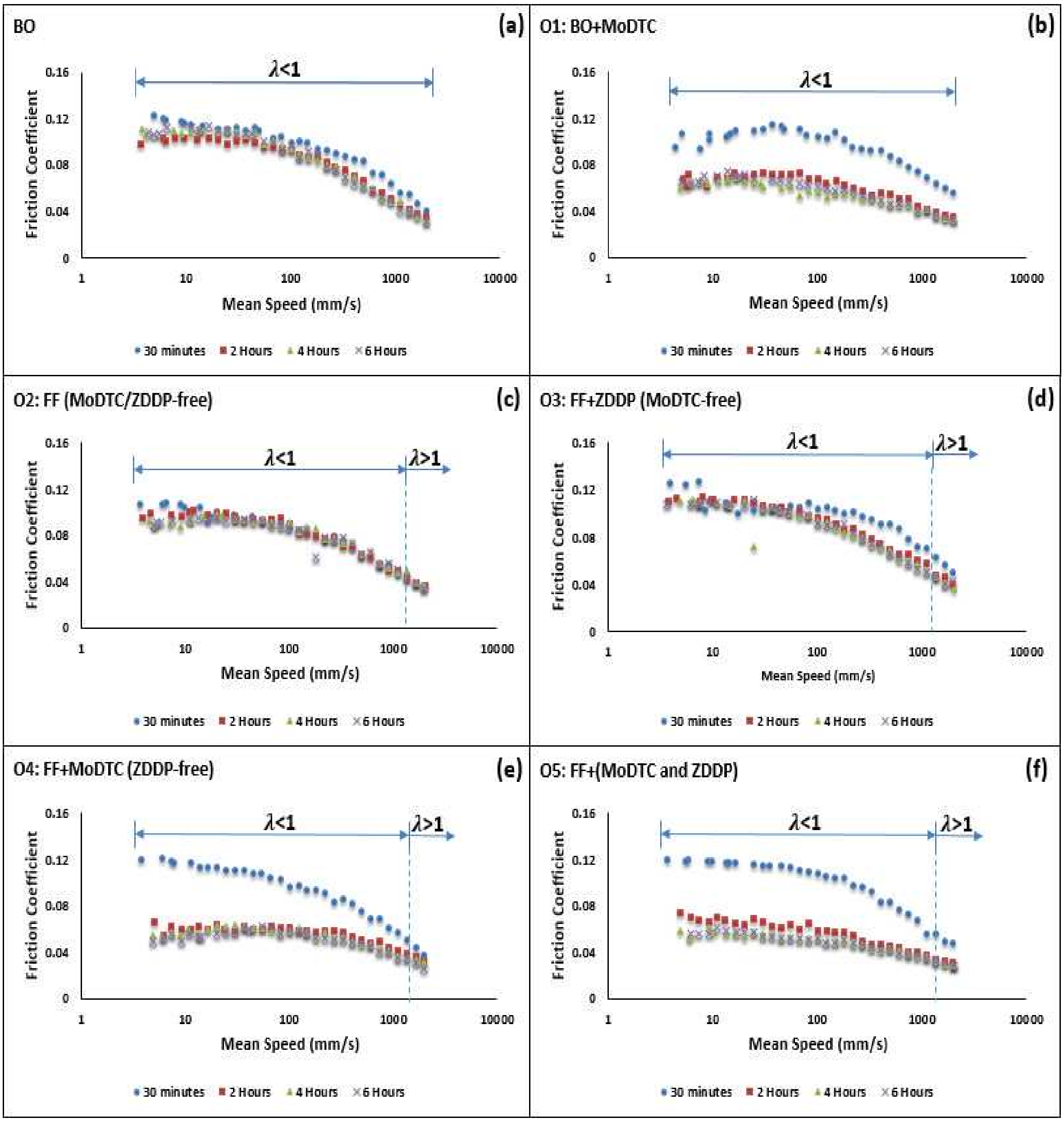

Fig. 5. Stribeck curves for (a) BO, (b) O1, (c) O2, (d) O3, (e) O4 and (f) O5 as a function of time at 200% SRR

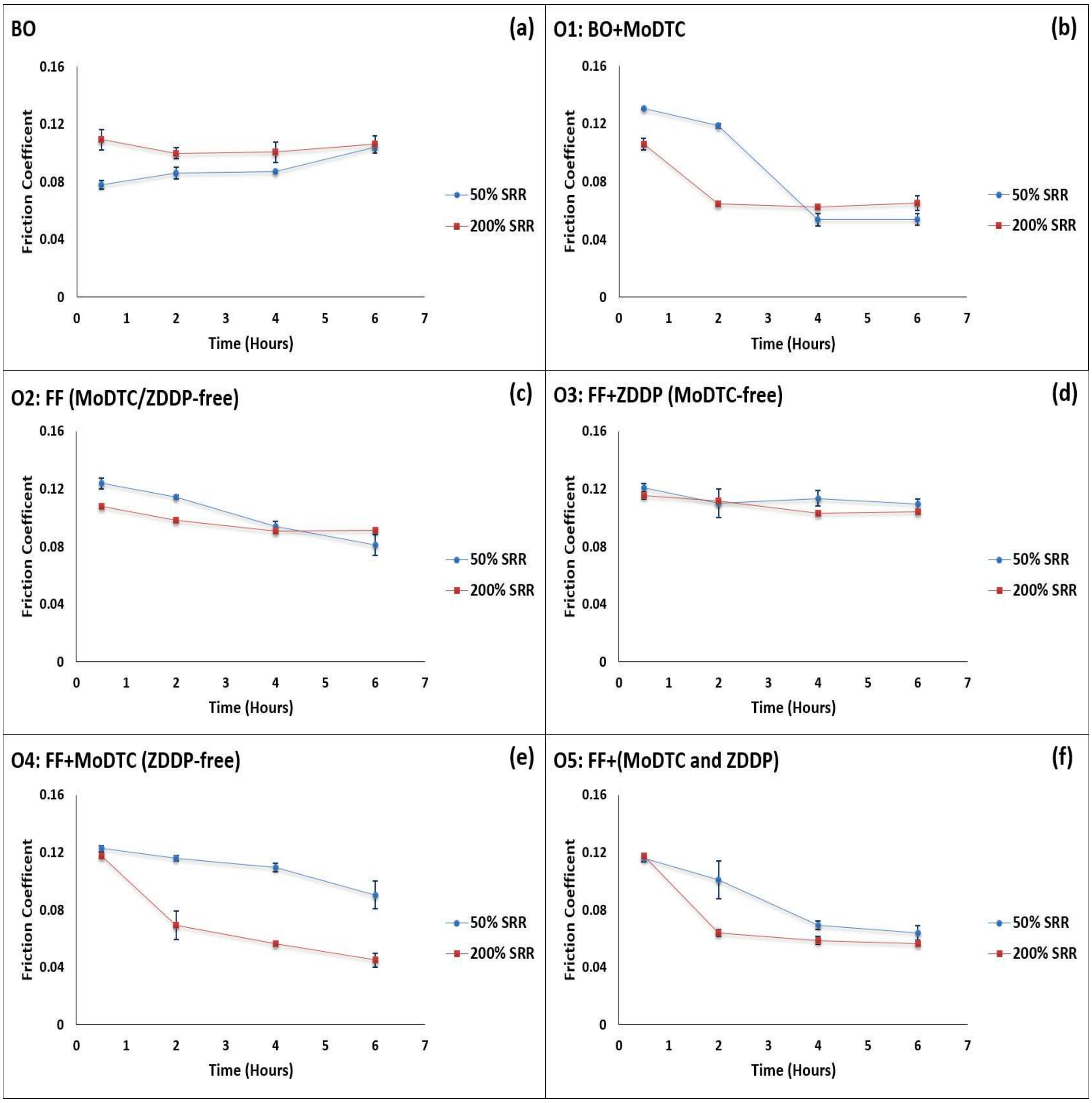

Fig. 6. Friction coefficients for (a) BO, (b) O1, (c) O2, (d) O3, (e) O4 and (f) O5 at mean speed = 10 mm/s under 50% SRR and 200% SRR

Table 3: Range of surface roughness for balls and discs at the end of each test

Oil Type	Roughness, R_q (μm)			
	50% SRR		**200% SRR**	
	Disc	**Ball**	**Disc**	**Ball**
BO	0.22-0.36	0.05-0.31	0.13-0.12	0.09-0.20
O1: BO+MoDTC	0.11-0.29	0.10-0.15	0.15-0.20	0.09-0.31
O2: FF(MODTC/ZDDP-free)	0.19-0.21	0.03-0.16	0.20-0.22	0.09-0.32
O3: FF+ZDDP (MoDTC-free)	0.14-0.15	0.11-0.13	0.12-0.30	0.07-0.11
O4: FF+MoDTC(ZDDP-free)	0.13-0.27	0.04-0.13	0.23-0.37	0.03-0.11
O5: FF+(MoDTC+ZDDP)	0.11-0.17	0.12-0.16	0.13-0.20	0.09-0.33

4.1.3. Range of friction values in the boundary lubrication regime

Table 4 shows how the addition of MoDTC affects steady state friction values for the DLC/CI system when lubricated in base oil, fully formulated (FF) oil without ZDDP and fully formulated oil with ZDDP under boundary lubrication regime. From Table 4, it is apparent that regardless of the type of contact, the addition of MoDTC to the oil formulations always improved the frictional properties of the DLC/CI system. In the case of fully formulated oil B containing ZDDP (i.e. O3 and O5), it can be seen that the positive effect of MoDTC on reducing friction was more pronounced for the pure sliding contact.

The range of friction values ($\Delta\mu$) is defined as the difference between the highest friction value (i.e. at the start of the test) for each test duration and the lowest friction value under the boundary lubrication regime (i.e. when $\lambda<1$). $\Delta\mu$ values for all lubricants and for different time intervals throughout the tests are plotted in Fig. 7. From Fig. 7 (a), at 50% SRR, MoDTC offered the highest friction reduction for the first 2 hrs for O1 and O5 while the highest friction reduction was observed for O4 when the test ran for 4 hrs. Fig. 7 (b), at 200% SRR, the effect of MoDTC on friction reduction was considerable during the running-in period (i.e. initial 30 minutes). Interestingly, the range of friction values for the lubricant with ZDDP alone was quite constant and was not affected over time. It is clear that friction coefficient values were observed to vary quite considerably for most of the lubricants. This is quite an important finding as most of the modelling works assume a constant value for (μ) across the boundary lubrication regime [28]. In practice, however, friction values may vary due to the changes in surface physical, chemical and mechanical properties. In addition, surface topography experiences significant modifications due to different surface phenomena which can lead to fluctuations in friction.

Table 4: Average of steady state friction in boundary lubrication at the last hour of each test

Oil Type	Average of steady state friction coefficients when λ<1			
	50% SRR		**200% SRR**	
	Without MoDTC	**With MoDTC**	**Without MoDTC**	**With MoDTC**
BO	0.08	0.05	0.09	0.06
FF (free of ZDDP)	0.08	0.07	0.09	0.06
FF + ZDDP	0.1	0.06	0.1	0.05

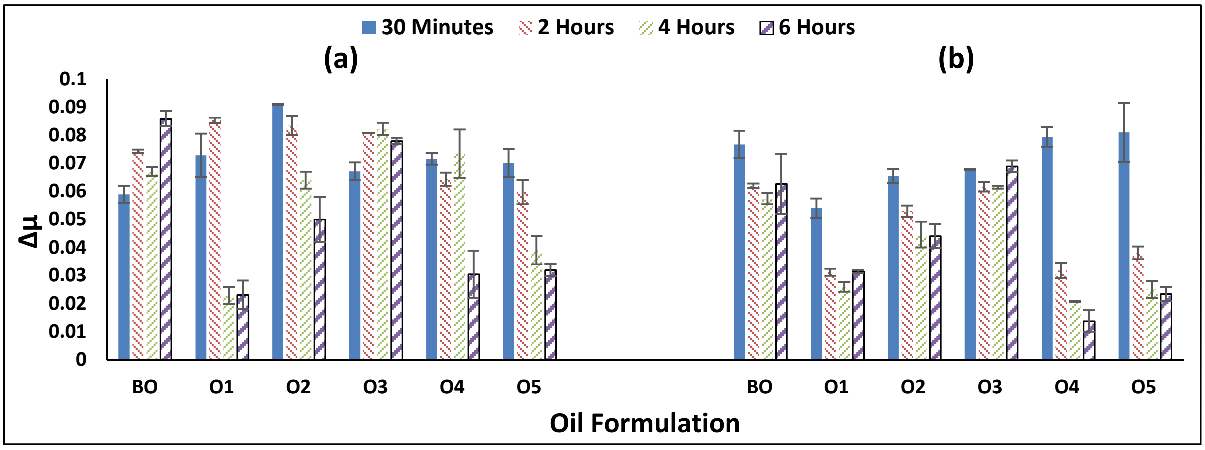

Fig. 7. Range of friction values at λ <1 for all oils: (a) at 50% SRR and (b) at 200% SRR

4.2. Wear results

Post-test physical observation of DLC balls by optical microscope indicated a very shallow wear scar on all balls irrespective of the oil formulation which made the quantitative analysis of the wear scar on all DLC balls a challenge. In order to quantify the wear depth of the coated balls and CI disks, White Light Interferometer (WLI) was used. Representative images of the wear track that formed on both the CI disk and the DLC coated ball are shown in Fig. 8. Furthermore, wear depths for both the discs and the balls were evaluated and shown in Fig. 9. It is important to observe that no lubricants show extremely high wear on DLC coating. In addition, the uncoated cast iron discs exhibited more wear than the DLC coated balls, as expected, because of the large difference in hardness. This is in line with other published literature where they found lower wear of the DLC coated balls as compared to the uncoated disk [14, 31, 32].

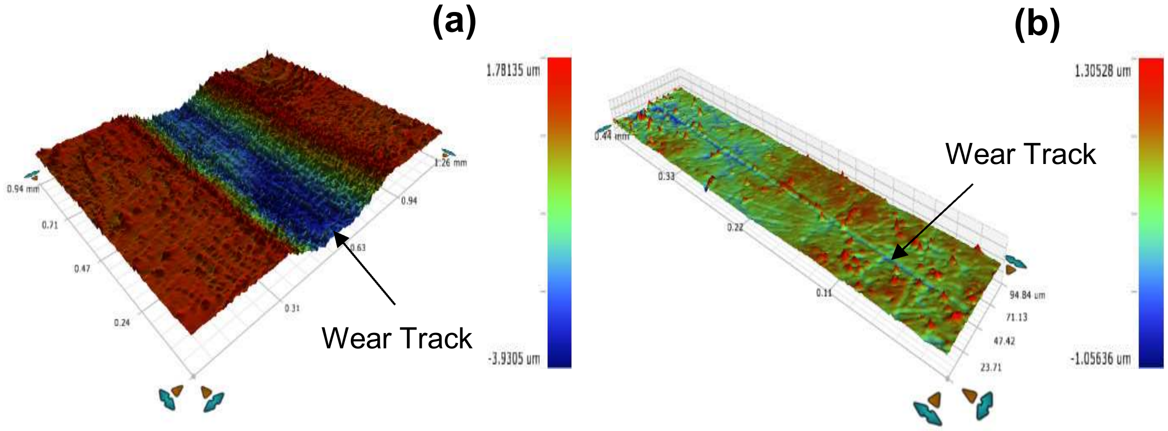

Fig. 8. Representative interferometer images of the wear track that formed on: (a) uncoated cast iron disc and (b) DLC coated ball

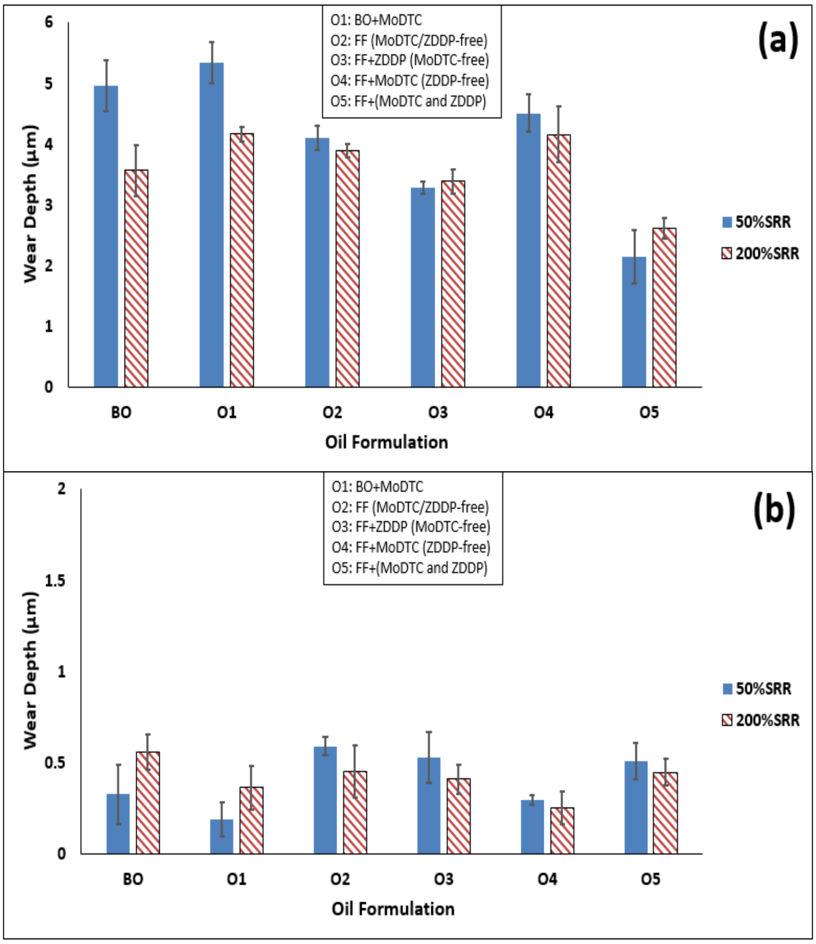

Fig. 9. Average of wear depths that formed on: (a) uncoated cast iron discs and (b) DLC coated balls (note different wear depth scales)

4.3. Chemical analysis of tribofilm

4.3.1. SEM-EDX

From Fig. 10, SEM micrographs of the CI discs revealed that interactions took place among the oil formulation, type of contact, the disc surface and the DLC ball surface. However, the DLC balls were not clearly identified by SEM and the micrographs were seen to be similar under the effect of contact type and oil formulation.

EDX semi-quantification of CI discs and DLC balls (for Mo, Zn, P and S elements) is presented in Fig. 11. Essentially, the chemical composition of the tribofilms was found to vary with changing the type of contact and the oil formulation. Generally, greater Mo, Zn, S and P was reported on CI discs than DLC balls. This reveals that the tribofilm formed on the CI discs was thicker than the tribofilms formed on the DLC balls. Similar findings were seen by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

Comparing sliding/rolling contact to pure sliding contact, the CI disk lubricated in O1 showed similar characteristics under both contacts. Nevertheless, low friction and good wear was observed under pure sliding contact. This clearly confirms that the tribological performance was not only controlled by the tribofilm formed on the surface but also by the contact type. Although quite similar amounts of Mo were detected on the CI discs (lubricated in O4) under both contacts, a clear reduction in friction was reported under pure sliding contact. For the DLC balls lubricated in O1, O4 and O5, only Mo was seen while no other elements (i.e. Zn, S and P) were detected under both contacts.

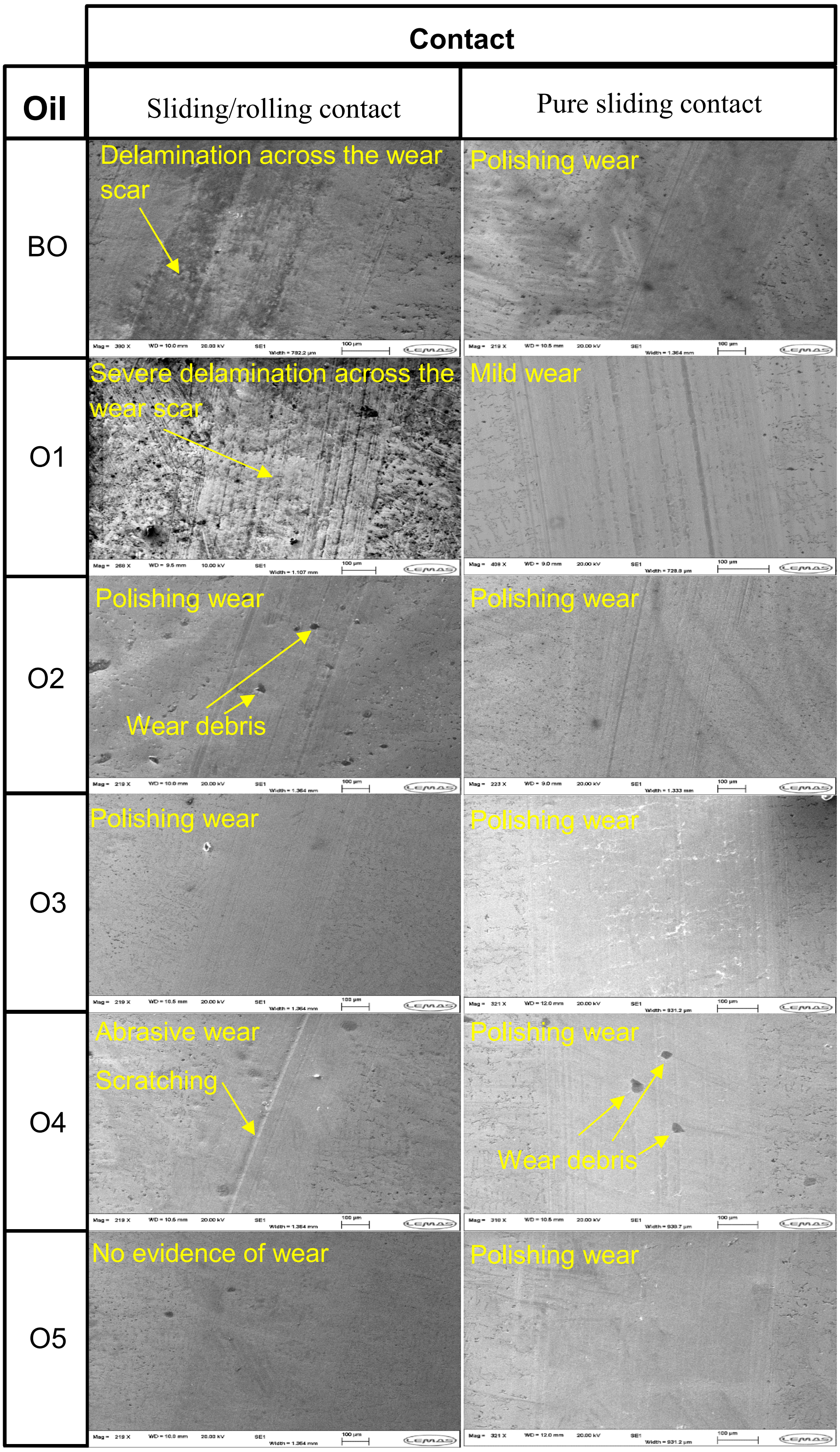

Fig. 10. SEM micrographs of CI disks at end of test

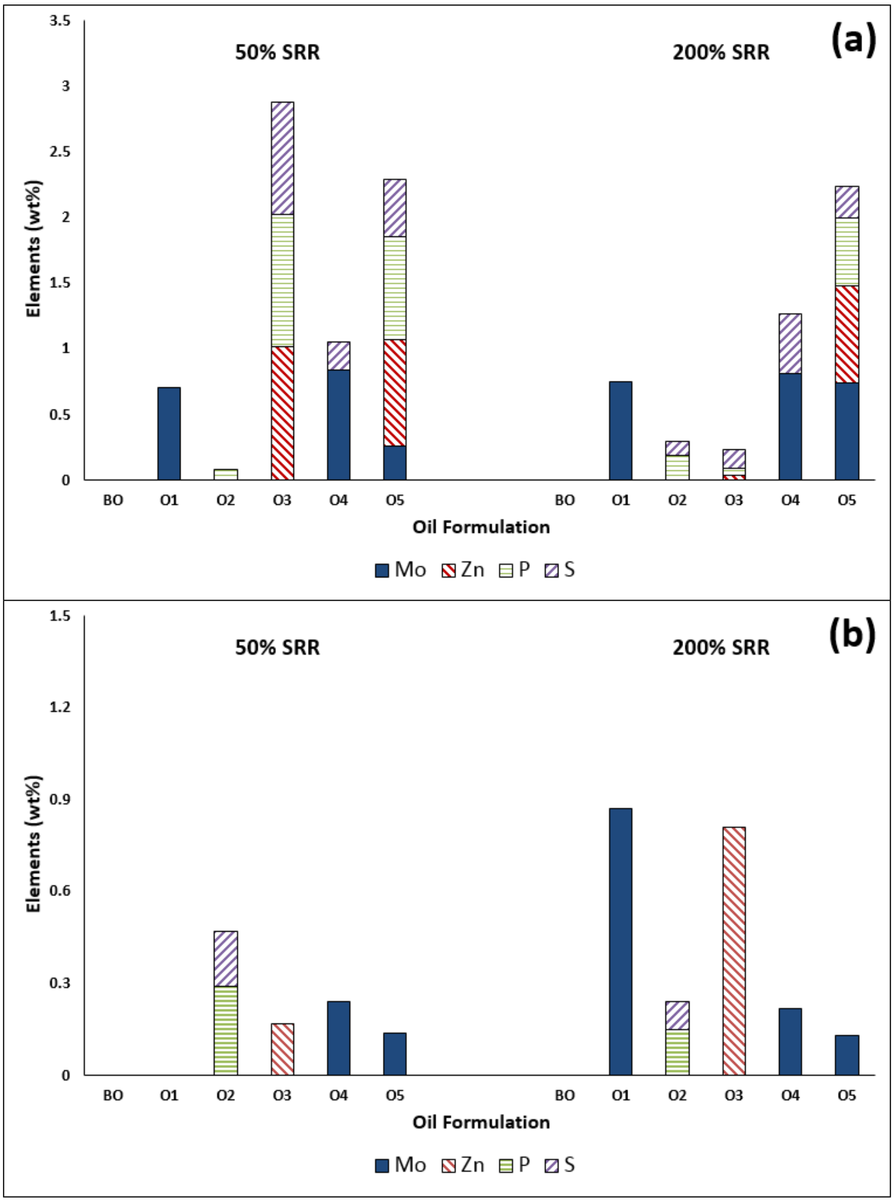

Fig. 11. EDX semi-quantification of regions inside the wear track balls under both contacts on: (a) uncoated cast iron discs and (b) DLC balls (note different wt% scales)

4.3.2. Raman spectroscopy

Based on the literature, the expected shift in Raman spectroscopy for molybdenum disulfide (MoS_2) is reported at 383-410 cm^{-1}, molybdenum trioxide (MoO_3) at 828-951 cm^{-1}, carbon (C) at 1366-1596 cm^{-1}, haematite (Fe_2O_3) at 120-310 cm^{-1} and magnetite (Fe_3O_4) at 670-680 cm^{-1} [4, 33-35]. Raman spectra obtained from the CI discs under both contacts is shown in Fig. 12. Raman spectra are plotted on the same scale and have been shifted vertically for clarification purposes. For the CI disks lubricated with MoDTC additive (i.e. O1, O4 and O5), the Raman spectra under sliding/rolling contact indicated the presence of MoS_2 in the range of (380-413 cm^{-1}). For all lubricants containing MoDTC, MoO_3 was not detected by Raman spectroscopy. The broad peaks at 925-926 cm^{-1} were assigned to the iron (II) molybdate $FeMoO_4$ [2, 4]. The iron molybdate is clearly detected when using O1 while there was little presence of $FeMoO_4$ when using O4 and O5. Due to the graphite normally present in the microstructure of the cast iron, peaks due to the formation of graphitic carbon are observed on the CI disc surface. The G and D peaks were around 1595 cm^{-1} and 1367 cm^{-1} respectively. However, carbon peaks were not clearly pronounced when using O1, O2 and O5 as compared to the CI disks lubricated in BO, O3 and O4. Fe_2O_3 peaks (197-299 cm^{-1}) were observed for BO, O1, O4 and O5. In addition, Fe_3O_4 was clearly detected in the range of (671-685 cm^{-1}) when using BO, O1, O3 and O4. In contrast, there was no presence of Fe_2O_3 and Fe_3O_4 for all lubricants under pure sliding contact.

Figure 13 shows the intensity of MoS_2 and $FeMoO_4$ for all oils containing MoDTC (i.e. O1, O4 and O5) under both contacts. Comparing pure sliding contact to sliding/rolling contact, higher intensity of MoS_2 (385-411 cm^{-1}) was clearly observed. This is in agreement with the friction results (i.e. lower friction was reported for O1, O4 and O5 under pure sliding contact as compared to sliding/rolling contact). In addition, for pure sliding contact, $FeMoO_4$ (925 cm^{-1}) was only detected when using O1. Raman peaks due to the presence of carbon (1595 cm^{-1}-1367 cm^{-1}) were not observed when using O4 and O5.

On the other hand, for both contacts and for all lubricants used in this study, Raman spectra for the DLC balls have shown similar characteristics or film structures (i.e. no structural modifications have occurred), as shown in Fig. 14. Carbon peaks were the only peaks that clearly indicated on the DLC ball surface. The G and D peaks were around 1550 cm^{-1} and 1370 cm^{-1} respectively. For the G peak, under both contacts, the Raman spectra showed no difference in the value of the full-width at half-maximum (FWHM) and the value of the ratio H_D/H_G. This might suggest that no structural modification of the DLC balls has happened after 6.5 hrs test duration. However, based on EDX results, Mo was detected in most DLC balls lubricated with MoDTC additive (i.e. O1, O4 and O5). Nevertheless, no MoS_2 and/or MoO_x peaks were observed on the DLC balls. This could either be due to a low amount of tribofilm formed or the surface sensitivity of the Raman Spectroscopy. Therefore, to confirm previous findings, all samples were examined using X-ray photoelectron spectroscopy (XPS). Details of this is discussed in the next section.

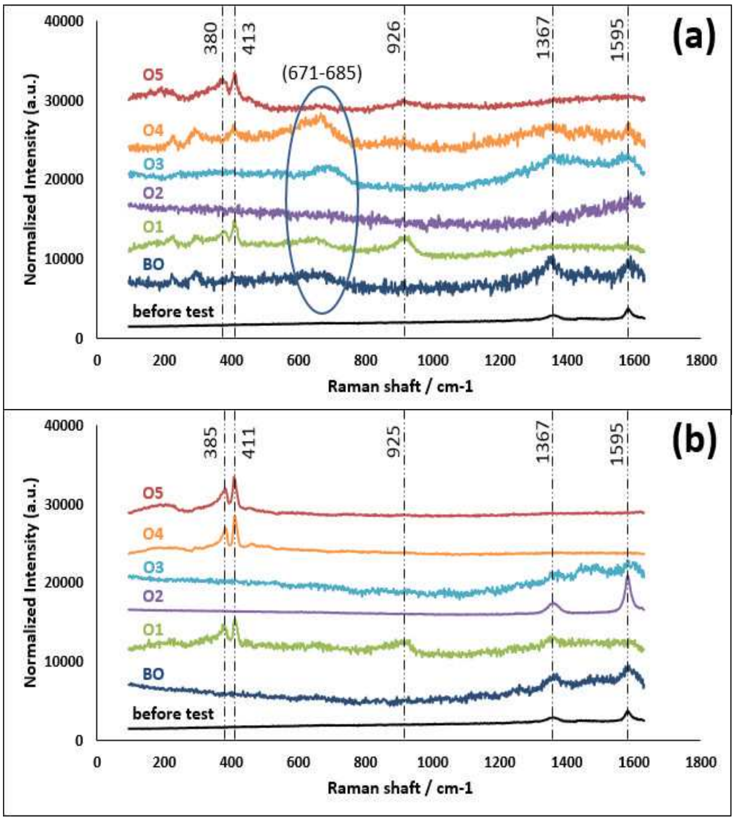

Fig. 12. Raman spectroscopy for the CI discs under: (a) sliding/rolling contact, (b) pure sliding contact

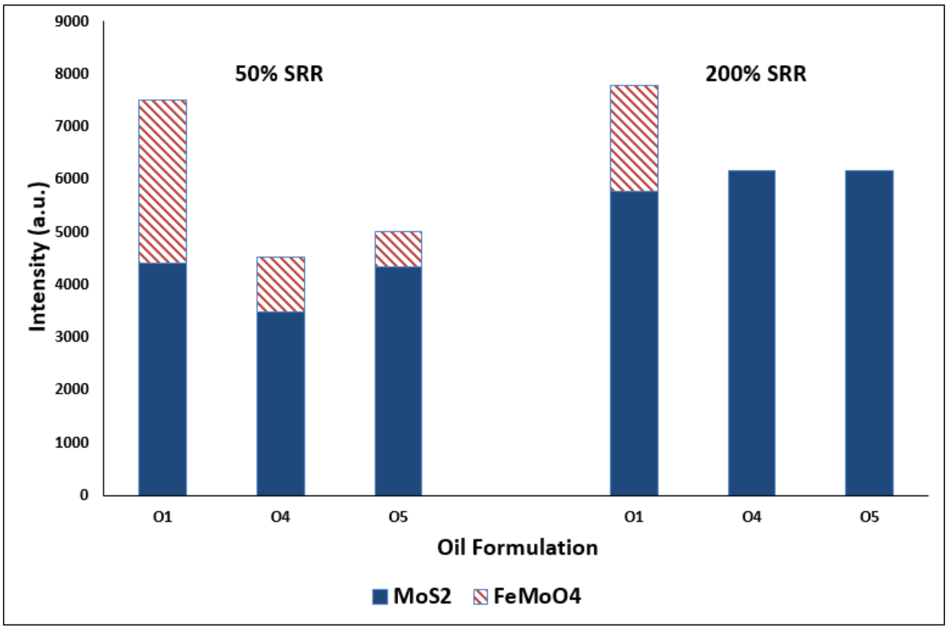

Fig. 13. The intensity of MoS_2 and $FeMoO_4$ for the CI discs under both contacts

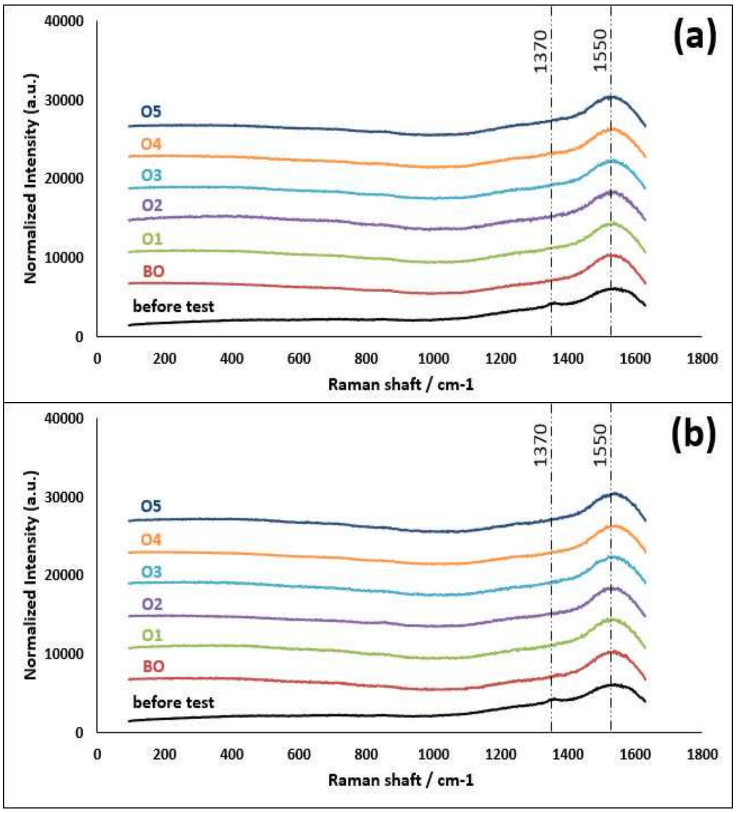

Fig. 14. Raman spectroscopy for the DLC coated balls under: (a) sliding/rolling contact, (d) pure sliding contact

4.3.3. XPS

From previous XPS analyses, tribofilms of lubricants containing MoDTC showed Mo 3d peaks at 229, 232.3 and 235 eV [36, 37]. The tribofilms of lubricants containing MoDTC were thought to be composed of MoO_3 because of the presence of Mo $3d_{5/2}$ peak at 232.3 eV. The Mo $3d_{5/2}$ peak for $FeMoO_4$ is also reported at 232.3 eV [38, 39]. As molybdenum in MoO_3 and $FeMoO_4$ have the same oxidation state (+6), it is impossible to distinguish the two compounds (i.e. MoO_3 or $FeMoO_4$) from XPS analysis [4]. However, Raman spectroscopy is capable of clearly distinguishing molybdenum species, even if these species have the same oxidation state. Thus, MoO_3 or $FeMoO_4$ peaks were clearly distinguished from Raman analysis [40, 41]. In this work, Raman peaks belonging to $FeMoO_4$ were clearly observed but MoO_3 peaks were not detected at all. Therefore, for the XPS results, it was believed that the Mo $3d_{5/2}$ peaks are due to the presence of $FeMoO_4$ and not MoO_3 [4].

For both contacts, the fitted Mo 3d peaks obtained from the CI discs lubricated in oils containing MoDTC (i.e. O1, O4 and O5) are shown in Fig. 15. Unlike Raman results, it can be seen that regardless of the contact type, $FeMoO_4$ and MoS_2 were all identified in the tribofilms formed on the CI disks. For all lubricants, the $MoS_2/FeMoO_4$ ratio was higher under pure sliding contact compared to sliding/rolling contact. It is also evident that the quantity of Mo, as detected by the Mo 3d peak on the CI disk under pure sliding contact was higher for O5 compared to O1 and O4. That could explain the friction values which were found to be the lowest when using O5. From Fig. 15, it is also evident that $FeMoO_4$ was not detected on the disc before test, this confirms that $FeMoO_4$ come from the tribofilm, not the original surface. For both contacts, the XPS spectra of ZDDP derived species (Zn 2p and P 2p) formed on the CI disks using O3 and O5 are shown in Fig. 16. It can be seen that Zn-phosphate and ZnS/ZnO species were formed on the CI discs under both contacts.

Unlike the Raman spectra on the DLC balls, XPS spectra showed that $FeMoO_4$ and MoS_2 were generally observed on the tribofilms formed on the DLC balls. For both contacts, the fitted Mo 3d peaks obtained from the DLC balls lubricated in oils containing MoDTC (i.e. O1, O4 and O5) are shown in Fig. 17. It was evident that the intensity of $FeMoO_4$ was higher under sliding/rolling contact as compared with the pure sliding contact. For O5, the amount of Mo 3d detected on the tribofilm formed on the DLC was higher under pure sliding contact compared to the sliding/rolling contact. This result validates the friction results obtained by the DLC ball under sliding/rolling contact. For both contacts, the XPS spectra of ZDDP derived species (Zn 2p and P 2p) formed on the DLC balls using O3 and O5 is shown in Fig. 18. It can be seen that the formation of the phosphate film was not affected by the presence of MoDTC. For O5, the amount of Zn 2p and P 2p detected on the DLC ball was slightly higher under pure sliding contact compared to the sliding/rolling contact. The obtained results could justify the wear performance of the DLC ball under pure sliding contact. For both contacts, the fully formulated lubricant (O5), which contains MoDTC and ZDDP, has shown the best tribological performance (i.e. lower friction and wear) of all the tested lubricants. XPS depth profiling for O5 only for both contacts is shown in Fig. 19. For clarification purposes, Fig.19 is plotted on different scales. For both contacts, the tribofilm formed on the CI discs was relatively thicker than the tribofilms formed on the DLC balls.

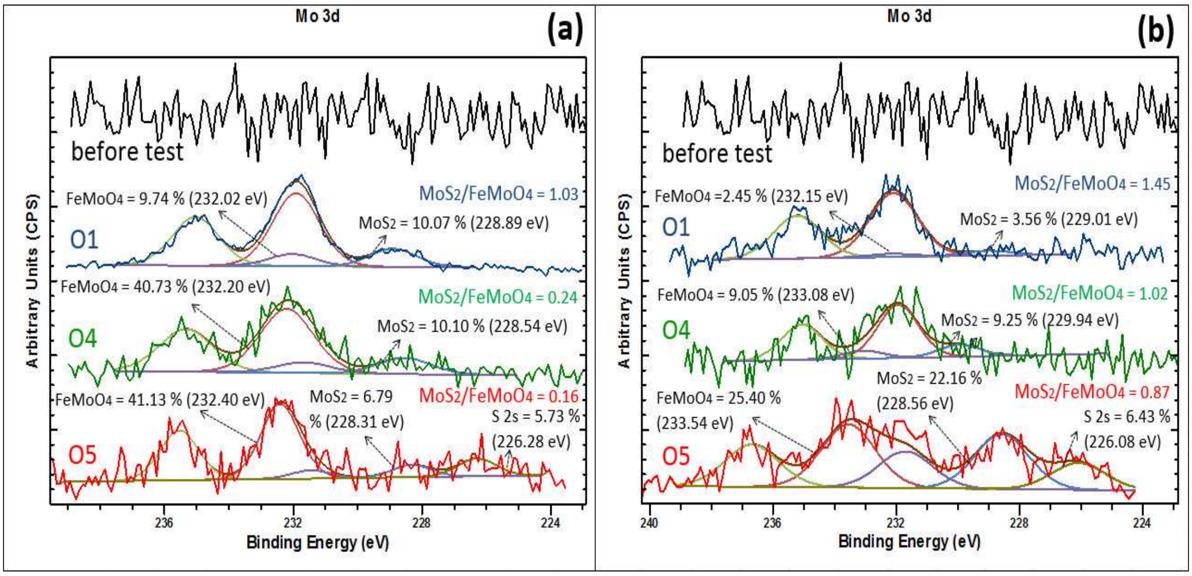

Fig.15. XPS spectra of the discs lubricated with MoDTC under: (a) sliding/rolling contact, (b) pure sliding contact

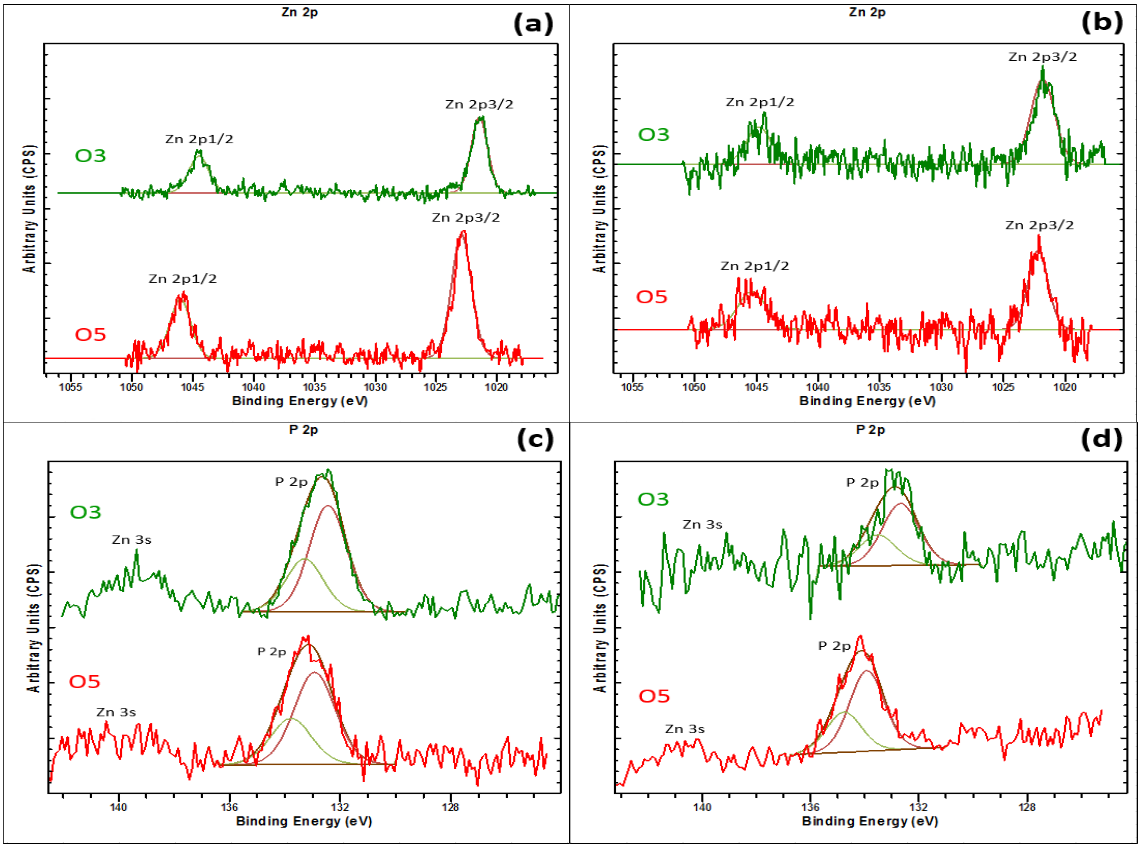

Fig. 16. XPS spectra of the discs lubricated with ZDDP: (a) Zn 2p under sliding/rolling contact, (b) Zn 2p under pure sliding contact, (c) P 2p under sliding/rolling contact, (d) P 2p under pure sliding contact

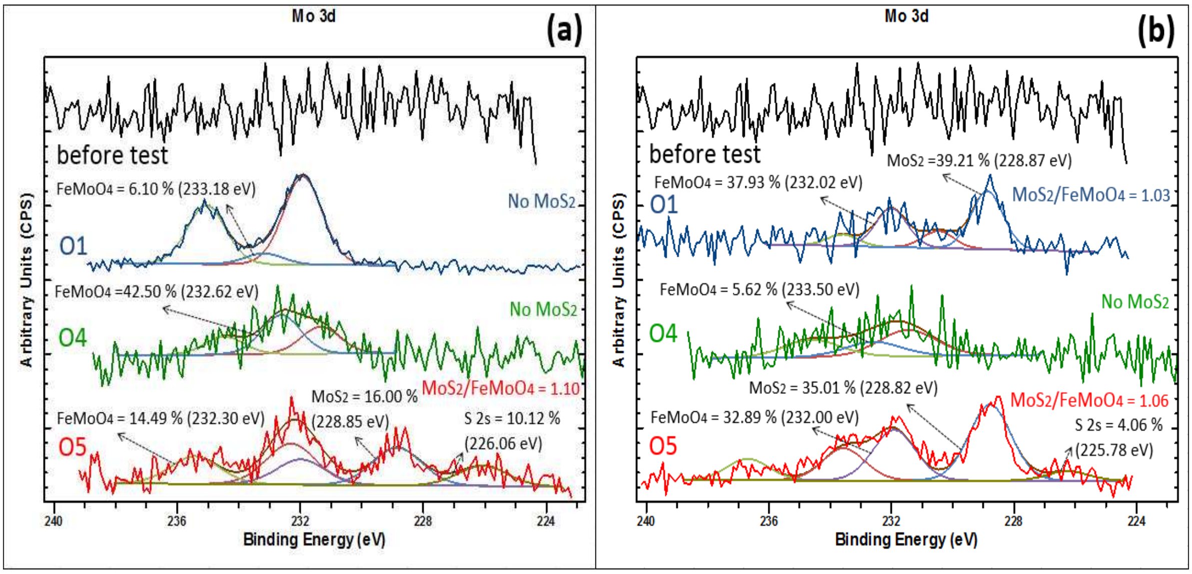

Fig. 17. XPS spectra of the balls lubricated with MoDTC under: (a) sliding/rolling contact, (b) pure sliding contact

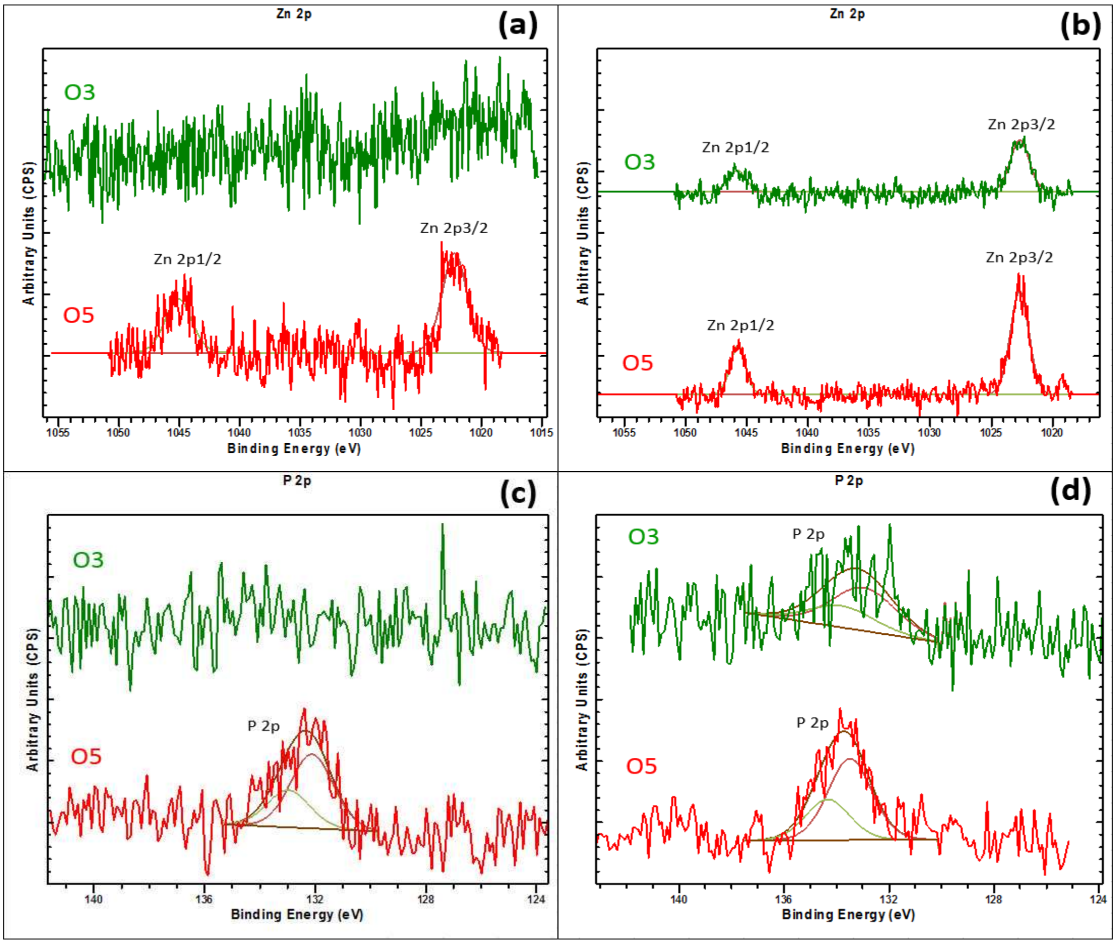

Fig. 18. XPS spectra of the balls lubricated with ZDDP: (a) Zn 2p under sliding/rolling contact, (b) Zn 2p under pure sliding contact, (c) P 2p under sliding/rolling contact, (d) P 2p under pure sliding contact

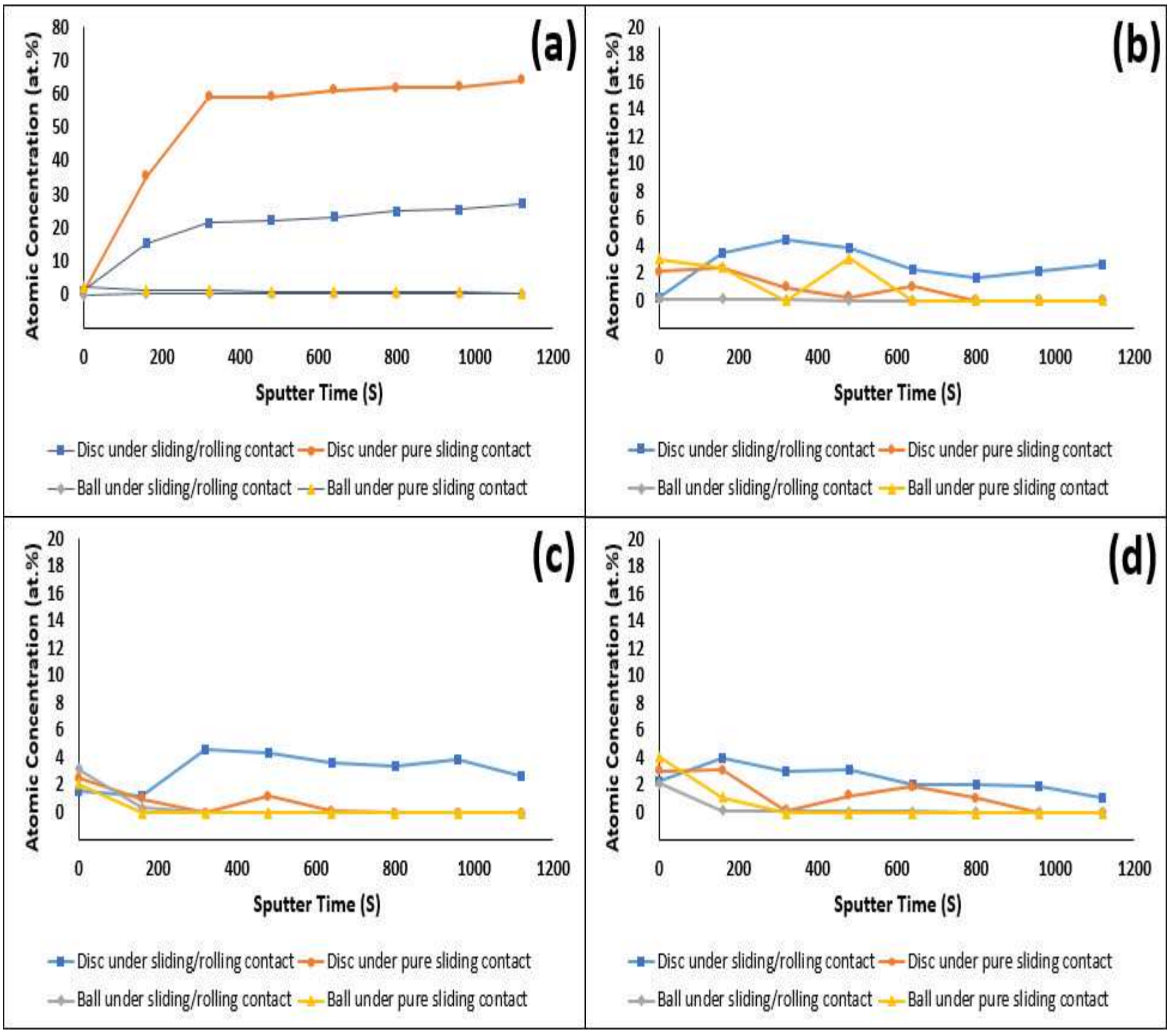

Fig. 19. Depth profiles of the discs and balls lubricated in O5: (a) Fe, (b) Zn, (c) P, (d) Mo (note different at. % scales)

5. Discussion

5.1. Effect of oil formulation and contact type on Stribeck curve evaluation

For 50% SRR (see Fig. 4), it is clear that most of the lubricants showed a low friction coefficient of about 0.04 at high entrainment speed, characteristic of the mixed lubrication regime. The lubricant film provides partial separation; the contact load is shared between the contacting asperities and the film as a result of some mechanical interactions [42, 43]. At low entrainment speed, however, all of the lubricants showed higher friction, characteristic of the boundary lubrication regime, where extensive interactions occur and behaviour is characterised by the formation and removal of thin films of molecular proportions called tribofilms [44]. In the absence of additives, BO exhibited fluctuating friction values over varying entrainment speeds. MoDTC has no clear effect on friction reduction for the first 30 minutes of the tests; probably because the MoS_2 sheets need a sufficient time in order to be completely formed, as reported by Grossiord *et al.* [36] and Rai *et al.* [45]. BO gave the lowest friction among all other oil formulations for speeds ranging from 5 to 330 mm/s. Friction values were slightly reduced after 2 hrs of rubbing for all oil formulations and the reduction in friction was particularly significant for O5, probably due to a synergy between MoDTC and ZDDP. This is in line with the literature where MoDTC was found to be more effective when used together with the ZDDP and the combination of both was reported to significantly improve the tribological performance [46]. BO still exhibited fluctuating friction values after 2 hrs of rubbing, likely due to the absence of additives. Early work [36, 47, 48] has shown that the MoDTC additive readily forms MoS_2 sheets under mixed-boundary lubrication regimes offering low friction on the tribological contacts. As a result, MoDTC played an essential role in reducing friction after 4 hrs of rubbing; O1 and O5 showed a higher friction reduction when compared to the rest of the oil formulations. Stable friction was reported after 6 hrs of rubbing. O3 gave the highest friction among all other oil formulations for speeds ranging from 5 to 530 mm/s. This is in line with the literature where tribofilms formed by ZDDP showed higher friction performance [49]. ZDDP increases friction when added to the lubricant due to the formation of pad-like tribofilm. For pure sliding (200% SRR) contact (see Fig. 5), it is apparent that the effect of MoDTC and ZDDP in the first 30 minutes of rubbing is negligible. This is mainly because tribofilms of both additives need sufficient time to form on the surface. The lowest friction was about 0.03 which resulted from O2 and is characteristic of the mixed lubrication regime. One similarity between base oil and ZDDP alone was that BO and O3 gave the highest friction of about 0.1, probably due to the absence of additives in BO and the presence of ZDDP in O3. The effect of both MoDTC and ZDDP additives was more pronounced after 2 hrs of rubbing which led to a lower friction response. For this contact (i.e. pure sliding) O3 still showed the highest friction which was likely due to the presence of ZDDP.

5.2. Effect of MoDTC on wear

From Fig. 9-a, cast iron discs showed relatively high wear when lubricated with O1 and O4 (i.e. MoDTC alone), suggesting a negative effect of MoDTC in increasing wear of a ferrous counterpart rubbed against a DLC coating [14]. In line with the literature, the interaction between MoDTC and ZDDP at O5 gave the lowest wear to the CI disk [7]. ZDDP in O3, as expected, played a key role in reducing wear of the CI disk. In the absence of ZDDP (i.e. BO, O1, O2 and O4), sliding/rolling contact appears to exhibit more wear than pure sliding contact on the CI disks, suggesting that the wear reduction is not only controlled by the oil chemistry but also by the type of contact. That could be attributed to a slower build-up of tribofilms for the sliding/rolling contact compared to the pure sliding contact. Some previous works [3, 11-13] have reported high wear of DLC coatings in presence of MoDTC. In contrast, very limited studies showed reduction in wear of a DLC coating when lubricated with MoDTC additive. Vengudusamy *et al.* [14] observed that MoDTC reduces wear in most of his tests in DLC/DLC contact and a few tests in DLC/steel contacts. In this study, from Fig. 9-b, it is clear that no lubricants show extremely high wear on the DLC coating. For the DLC balls lubricated with MoDTC additive, a ferrous surface (i.e. CI disc) was expected to help in increasing the wear of the DLC coating if iron oxide particles are presented in the DLC/cast iron interface [17]. However, in the absence of ZDDP, DLC coated balls showed quite low wear when MoDTC was present in the oil formulation (i.e. O1 and O4). Tung *et al.* [50] studied DLC/cast iron contacts and also reported that MoDTC reduces wear of a DLC coating in a formulated engine oil. There is however no evidence whether the formulated lubricants in Tung *et al.* [50] contained ZDDP or not, as this anti wear additive could supress the effect of MoDTC on promoting wear of DLC coatings [13]. Comparing O3 with O2, the presence of ZDDP in the oil formulation reduced the wear of the DLC balls [32] but the wear reduction was not considerable. Sliding/rolling contacts for all formulated lubricants (except for BO and O1) exhibit relatively higher wear than pure sliding contact on the DLC coated balls. This suggests that the pure sliding contact probably facilitated the build-up of tribofilms on the interface which in turn resulted in an enhanced lubrication and thus reduced wear of the DLC balls.

5.3. Effect of contact type on tribofilm evolution

The XPS analyses showed that a tribofilm on both tribopairs is formed under both contacts. Unlike recent work [2], it was found that the SRR values used in this study did affect the surface chemistry (i.e. tribofilm build-up was seen to be influenced by the change in SRR). Table 5 summarises the effect of SRR on the tribofilms formed on the DLC coated balls (mainly when lubricated with O1 and O3). As can be seen from Table 5, for O1, the DLC ball under sliding/rolling contact mainly consisted of $FeMoO_4$. For the same oil under pure sliding contact, both MoS_2 and $FeMoO_4$ were detected on the DLC surface. This could justify the friction results where lower friction was reported under pure sliding contact as compared with the sliding/rolling contact. In addition, as the DLC ball under sliding/rolling contact mainly consisted of $FeMoO_4$, high wear was expected due to enhanced removal of tribofilms from the DLC ball. Lower wear was reported on the DLC ball under sliding/rolling contact, suggesting that the wear performance, in some cases, was controlled more by the type of contact than the oil formulation. For O3 (FF+ZDDP), both Zn 2p and P 2p were observed on the DLC ball under pure sliding contact while no such compounds were detected on the DLC ball under sliding/rolling contact. Therefore, higher wear rate was reported for sliding/rolling contact than the pure sliding contact. On the other hand, for tribofilms formed on the CI discs (see Fig. 15), it can be seen that the $MoS_2/FeMoO_4$ ratio varies for the type of contact. In addition, it was found that $MoS_2/FeMoO_4$ ratio links to friction performance (i.e. the increasing of $MoS_2/FeMoO_4$ ratio reduces the coefficient of friction).

Table 5: Effect of SRR on the tribofilms detected on the DLC coated balls using XPS

	Sliding/rolling contact	Pure sliding contact
O1	Mo 3d ($FeMoO_4$ only)	Mo 3d ($FeMoO_4 + MoS_2$)
O3	-	Zn 2p (Zn 2p1/2 + Zn2p3/2) + P 2p

Generally, for most CI discs and DLC balls, there was a considerable variation in the chemical composition of the tribofilm that formed under both contacts. As a result, film thickness was seen to be influenced by the change in SRR. From Fig. 19 and Table 6, the film formed on the CI disc lubricated in O5 (FF+ZDDP+MoDTC) showed that concentrations of elements under pure sliding contact are significantly lower nearer to the substrate with high concentration of iron as compared to sliding/rolling contact. However, for DLC balls under both contacts, the depth profiles were fairly similar (i.e. both having thinner tribofilms). In addition, it can be observed that on cast iron, the thickness depends on sliding/rolling ratio whereas on DLC it does not.

Table 6: XPS quantification of tribofilms on the CI discs and DLC balls lubricated in O5

Sputter time: 1120s		C 1s%	Fe 2p%	O 1s%	Ca 2p%	Mo 3d%	Zn 2p%	P 2p%	S 2p%
Disc	50% SRR	20.7	27.2	37.7	5.9	1.0	2.5	2.7	2.0
	200% SRR	16.0	64.0	18.7	1.0	0	0	0	0
Ball	50% SRR	98.8	0	1.0	0	0	0	0	0
	200% SRR	97.7	0.1	1.6	0.4	0	0	0	0

6. Conclusions

The present study shows the tribological and tribochemical characteristics of a DLC/uncoated CI system with MoDTC-type friction modifier under sliding and rolling contacts. The main conclusions drawn from this work are:

- The sliding/rolling ratio affects friction, wear and tribochemistry in CI/DLC systems; pure sliding enhances MoDTC activation.
- Friction coefficient values were observed to vary across the boundary lubrication regime, unlike most modelling work which assume a constant value for coefficient of friction.
- The main MoDTC decomposition products are MoS_2 and $FeMoO_4$, not MoO_3. $FeMoO_4$ was identified as the reaction species, which is possibly responsible for the high friction.
- Tribofilm build-up is related to the sliding/rolling ratio (SRR). For instance, the DLC ball lubricated in base oil containing MoDTC (i.e. O1) created a film consisted of MoS_2 and $FeMoO_4$ under pure sliding contact while only $FeMoO_4$ was detected under sliding/rolling contact. In addition, for pure sliding contact, Zn 2p and P 2p were observed on the DLC ball lubricated in the presence of ZDDP additive (i.e. O3 and O5) while no such compounds were detected on the DLC ball under sliding/rolling contact. All these variations are supported by the friction and wear results.
- MoS_2/$FeMoO_4$ ratio played a key role in the tribological performance of the CI discs. MoS_2/ $FeMoO_4$ for CI discs lubricated in the presence of MoDTC additive (i.e. O1, O4 and O5) was higher under pure sliding contact as compared with sliding/rolling contact. This correlates with the obtained friction results.
- Regardless of the contact type, no lubricants showed high wear on DLC coating. In addition, all DLC balls showed thinner films compared to CI discs, so the tribofilms were hard to detect by Raman technique.

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