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Superlubricity of multilayer titanium doped DLC coatings by using low SAPS organic additives in base oil

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ABSTRACT

This study systematically investigates the tribological performance of titanium doped diamond-like carbon monolayer and multilayer coatings with superior mechanical properties. The coatings were lubricated in poly alpha olefin grade 4 (PAO4) base oil, containing three concentrations of two organic, ashless, and sulfur free (low SAPS) antiwear, and extreme pressure additives with different amounts of phosphorus and nitrogen (Duraphos® 178 and Duraphos® OAP). The multilayer Ti-doped DLC coatings exhibited superior tribological performance compared to uncoated steel, undoped DLC, and monolayer Ti-DLC coatings. They exhibited coefficient of friction values which were in the range of 0.013 and 0.006 (superlubricity) for formulations with Duraphos® OAP. Duraphos® 178 significantly lowered the specific wear rates of both the monolayer and multilayer coatings.

1. Introduction

To address the challenges posed by friction and wear in the current hyper industrialized era and to advance towards a sustainable tribological future, numerous solutions have been developed over the years. The reduction in friction and wear is necessary because it accounts for almost one fifth of the global energy consumption per annum [1], leading to significant resource depletion, increased carbon footprint, and additional cost for repairs and restoration of components. Importantly, with the electrification of vehicles and the rising demand for sustainable and green solutions, the need to reduce wear and friction has become more pressing than ever before. Furthermore, it is essential for environmental concerns that new solutions are implemented which are non-polluting and contribute towards Green Tribology and sustainability.

Among the solutions developed to reduce wear and friction, diamond-like carbon (DLC) coatings have emerged as one of the most promising solution [2]. These coatings are known for their high hardness, self-lubricating properties, wear resistance, low coefficient of friction (COF), and often biocompatibility. However, in their undoped form, they are relatively inert and do not readily interact with oil additives to form beneficial friction and wear reducing species [3]. While DLC coatings can be utilised under dry conditions to leverage their tribological properties [4], their full potential is realised in demanding applications when used in conjunction with lubricating oil formulations [5]. Achieving superlubricity, a condition where friction falls below 0.01 [6], is highly desirable when using DLC coatings.

Different kinds of lubricating base oils [7–15] containing additives are used to compose formulated oils for lubrication purposes. Pure base oils alone do not sufficiently react with the surface of undoped DLC coatings to form beneficial species between the rubbing surfaces, which is necessary to lower down the COF and specific wear rate (SWR). Therefore, various additives are added into the base oils to optimise their properties. These formulated oils enhance the tribological performance of DLC coated components in demanding applications. The primary additives include friction modifiers (FM), antiwear (AW), and extreme pressure (EP) additives. The most commonly used formulated oils consist of 95 wt.% base oil and 5 wt.% additives, often including sulfonated ash, phosphorus, and sulfur (SAPS) additives [16,17]. However, these additives pose significant environmental concerns, such as clogging catalytic converters, and their performance against DLC coatings is often inadequate [18,19]. It is desirable to use oil additives that

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Table 1
The composition of the oil formulations and their nomenclature for this work.

Base Oil	Additive	Additive's amount	Oil formulation name for this work
PAO 4	None	0	BO
PAO 4	Duraphos® 178	0.1 wt.%	BO−0.1−178
PAO 4	Duraphos® 178	0.2 wt.%	BO−0.2−178
PAO 4	Duraphos® 178	0.3 wt.%	BO−0.3−178
PAO 4	Duraphos® OAP	0.1 wt.%	BO−0.1-OAP
PAO 4	Duraphos® OAP	0.2 wt.%	BO−0.2-OAP
PAO 4	Duraphos® OAP	0.3 wt.%	BO−0.3-OAP

are organic and contain less or zero amounts of SAPS and avoid additives derived from heavy metals.

Even if the new organic low/zero SAPS oil additives are invented, undoped DLC coatings have a small chance for interaction with these additives because of their inert nature. To resolve this issue, the DLC coatings are doped. Among metal dopants for DLC, titanium (Ti) is one of the most significant dopants to enhance the tribological activity. Also, doping DLC with Ti (Ti-DLC) enhances several physical, thermal, and tribological properties of undoped DLC coatings [20–23].

Guo Y et al. [24] tested the tribological behaviour of Ti-DLC coatings (Ti concentration of 4 and 27 at.%, deposited by hybrid ion beam sputtering) under dry conditions and with pure PAO4 base oil (using a reciprocating test, with a counterbody of GCr15 having a diameter of 6 mm). Their results demonstrated that the coatings exhibited a lower COF when paired with the oil, compared to dry conditions. Additionally, they found that Ti doping in DLC reduced the wear rate of the coatings under oil-lubricated conditions. They concluded that PAO oil reduced the wear and friction for Ti-DLC coatings. They also claimed that COF was reduced due to the lubricious nature of oil and the formation of titanium oxide, whereas the wear was reduced as the wear debris were carried away by the oil, leaving a clean interface. The oil also hindered the formation of a transfer layer due to its flow. Furthermore, they related the H/E and H^3/E^2 values to explain the lower wear and friction in DLC coatings.

S Zhang et al. [25] deposited the Ti-DLC coatings, with Ti content ranging from 0 to 2 at.% on 316 L steel substrates. They conducted tribological tests in reciprocating motion against a counterbody of AISI 52100 steel. The coatings were tested with SAPS-based additives, leading to the conclusion that wear and friction are reduced when the Ti concentration exceeds 0.68 at.%. They also concluded that Ti provides the necessary activation energy for the coatings to chemically interact with phosphorous in the additives during rubbing.

In a study by Y Yang et al. [26], it was demonstrated that surfaces containing Ti, when react with the phosphate ester based oil additives, form a P-O-Ti layer on surface, which restricts the direct contact between the surface and the counterbody, thereby reducing wear and friction. Furthermore, it has been reported that ferrous surfaces, when interacting with phosphate esters additives, form a phosphorous and iron containing tribofilm. This tribofilm contributes to further wear and friction reduction [27,28]. Notably, incorporating an amine group into the chemical structure of phosphate esters significantly enhances the formation of these protective films [29,30]. However, literature has typically focused on either the Ti-containing surfaces or the ferrous counterbody surfaces, not examining them in conjunction.

Despite the improved tribological performance resulted from Ti doping in DLC coatings, the addition of Ti is known to compromise mechanical properties such as hardness (H) and elastic modulus (E). Our previous work [31] addressed these issues by depositing Ti-doped DLC coatings with a nanometric multi-layered structure having alternating layers of Ti-DLC and DLC. This approach preserved the mechanical integrity of the coatings, while mitigating the negative effects of Ti doping. The multilayered Ti-doped DLC coatings exhibited resistance to microcrack initiation and propagation during loading and sliding in tribological contacts [32,33]. The multilayer Ti-doped DLC coatings exhibited superior mechanical properties compared to the monolayer Ti-doped DLC coatings [31]. Both types of coatings had an average Ti concentration between 2.9 and 8.2 at.%, but the multilayer coatings consisted of alternating layers of undoped DLC and Ti-DLC. To achieve the average Ti concentration in the multilayer coatings identical to that in the monolayer coatings, the Ti-DLC layers had a significantly higher Ti content, ranging between 15 and 44 at.%. Due to these high Ti levels, it was expected to achieve superlubricity, as more Ti was available to react with the additives in the oil formulations [26]. The chemical state of Ti in the DLC coating was investigated using XPS, which revealed the formation of Ti-C and Ti-O bonds. However, these bonds did not lead to the formation of crystalline phases, as confirmed by both XRD and SAEDP analyses [31].

In practical applications, DLC coated parts typically have a counter surface composed of carbide forming elements like Fe and Ti. These counterbody materials facilitate the formation of stable tribofilms/transfer layers when tested against a DLC coated counterpart [34]. Bearing in mind the practicality and availability, we opted to use steel balls against DLC coatings rather than choosing a counterbody composed of exotic material(s) to achieve superlubricity. Additionally, to attain exceptional low friction performance, the DLC coatings are made highly hydrogenated, containing up to 40 at.% of hydrogen [34]. This can significantly reduce COF but at expense of inferior mechanical properties, namely lower H and E, as well as higher wear rates compared to non-hydrogenated DLC. The coatings we are reporting were practically non-hydrogenated, with a hydrogen content ranging from a minimum of 0.2 to a maximum of 0.7 at.% [31].

In this work, the tribological performance of Ti-doped DLC coatings is examined for three monolayer and three nanoscale multilayer coatings with identical Ti doping concentrations [31]. The PAO4 oil was used as the base oil with 0.1 - 0.3 wt.% of two AW and EP additives. Both additives were sulfur-free, ashless, and contained phosphorus to enhance tribological performance (low SAPS organic additives).

2. Materials and methods

2.1. Base oil and composition of oil formulations

PAO4 was used as the base oil both in its unformulated state and to make oil formulations for tribological testing. Its kinematic viscosity at 40 °C and 100 °C is approximately 17 cSt and 4 cSt ($100\ \text{cSt} = 1\ \text{cm}^2/\text{s}$), respectively. The PAO4 base oil was from Synfluid® - Chevron Phillips Chemicals.

For this study, two additives were used: Duraphos® 178 and Duraphos® OAP. Duraphos® 178, chemically named and formulated as 'C$_{12-14}$ - alkyl amine iso octyl phosphate – $C_{19}H_{42}NPO_4$ – $C_{29}H_{63}NPO_4$' [35], is an ester containing both phosphorus and nitrogen, with a phosphorous content of 5.95–8.17 wt.% and nitrogen content of 2.69–3.70 wt.%. It is registered under the CAS number 68187–67-7. Duraphos® OAP, known chemically as 'octyl acid phosphate – $C_8H_{19}O_4P$' [36], is also a phosphorus-containing ester but does not include nitrogen, containing 14.73 wt.% phosphorus and is associated with CAS numbers 39407–03-9/ 3991–73-9. These additives exhibit AW and EP properties (reduce both wear and friction), are ashless, sulfur-free, and contain phosphorus (low SAPS). They were yellow and had the characteristic odour of phosphorus-containing organic compounds. Duraphos® 178 had a viscous honey like consistency at room temperature. In contrast, Duraphos® OAP consistency was similar to PAO4 base oil. Both additives were manufactured by Solvay S.A. The base oil and additives for this study were provided by TOTAL Energies, Lyon, France, and they were used as received without further purification.

To evaluate the tribological properties of the DLC-based coatings,

Table 2
The specimens used in this work, including their main properties [31].

Disc Sample	Nature of sample	Thickness of coating (μm)	Ti at.%	H (GPa)	E* (GPa)	Residual stress (GPa)	Lc2 Adhesion (N)
M2 steel	Uncoated steel	N/A	N/A	63 HRC	213.6±3.1	N/A	N/A
DLC	DLC	1.51	0.0	16.2±0.6	184.8±5.9	−1.15±0.07	16.5±0.5
***m*Ti-DLC1**	Monolayer Ti-DLC	1.46	2.9	10.2±0.8	120.0±5.4	−1.05±0.05	23.5±4.8
***m*Ti-DLC2**		1.52	6.1	11.8±0.8	136.2±7.3	−1.24±0.03	23.4±1.6
***m*Ti-DLC3**		1.55	8.3	12.9±1.2	152.7±9.9	−1.54±0.16	23.5±2.3
***M*Ti-DLC1**	Multilayer Ti-DLC/DLC	1.50	2.9	13.3±1.1	151.7±7.5	−1.46±0.02	20.2±1.9
***M*Ti-DLC2**		1.52	5.9	15.7±1.5	170.5±6.6	−1.66±0.01	18.8±2.0
***M*Ti-DLC3**		1.65	8.2	12.7±0.9	147.8±6.1	−0.61±0.02	16.7±1.6

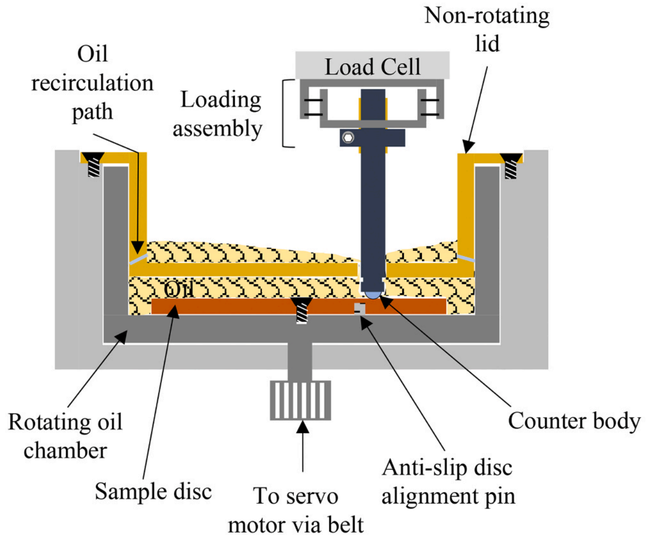

Fig. 1. Schematic of the tribometer apparatus used to evaluate tribological properties (figure is not according to scale).

pure PAO4 base oil and PAO4 base oil with three concentrations of each additive (0.1, 0.2, and 0.3 wt.%) were used. The composition of the oil formulations used for the tribological tests in this study and their nomenclature are provided in Table 1.

To prepare the oil formulations, PAO4 base oil was first poured into a clean glass beaker. The base oil was then heated from room temperature to 60 °C over 30 minutes while being magnetically stirred. After reaching 60 °C, the additive was introduced using a micropipette, and the solution was stirred further for 30 minutes at the same temperature. The formulated oil was then allowed to cool to the room temperature before their use in the tests. For each test, freshly prepared oil formulations were used without any storage after cooling down to the to room temperature.

2.2. *Coatings (discs) and counterbodies (balls)*

The DLC coatings deposited on the discs used in this work were developed according to the procedure defined in a previously published work [31], where the mechanical properties of these coatings were reported along with detailed structural analysis. One undoped DLC (as a reference), one set of three monolayer Ti-DLC coatings, and one set of three nanoscale multilayer Ti-DLC/DLC coatings were deposited by unbalanced direct current (DC) magnetron sputtering on quenched and tempered AISI M2 steel substrates after polishing the substrates. The monolayer and multilayer coatings had an identical overall chemical

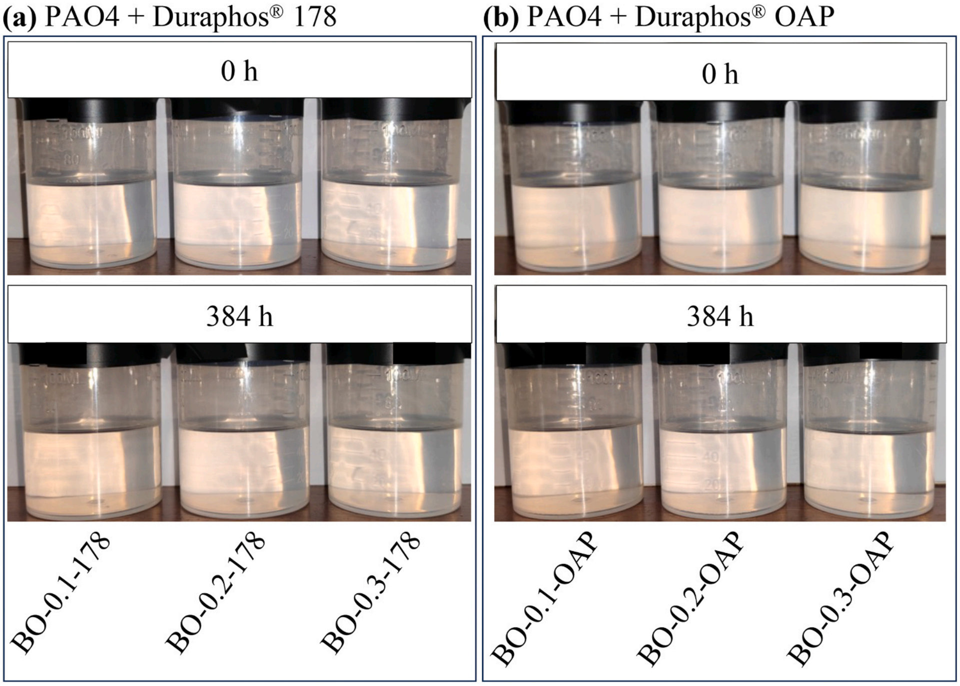

Fig. 2. The visual appearance of the oil formulations, both after their initial formulation and after a period of 384 hours: (a) Duraphos® 178 additive in PAO4 base oil, (b) Duraphos® OAP additive in PAO4 base oil.

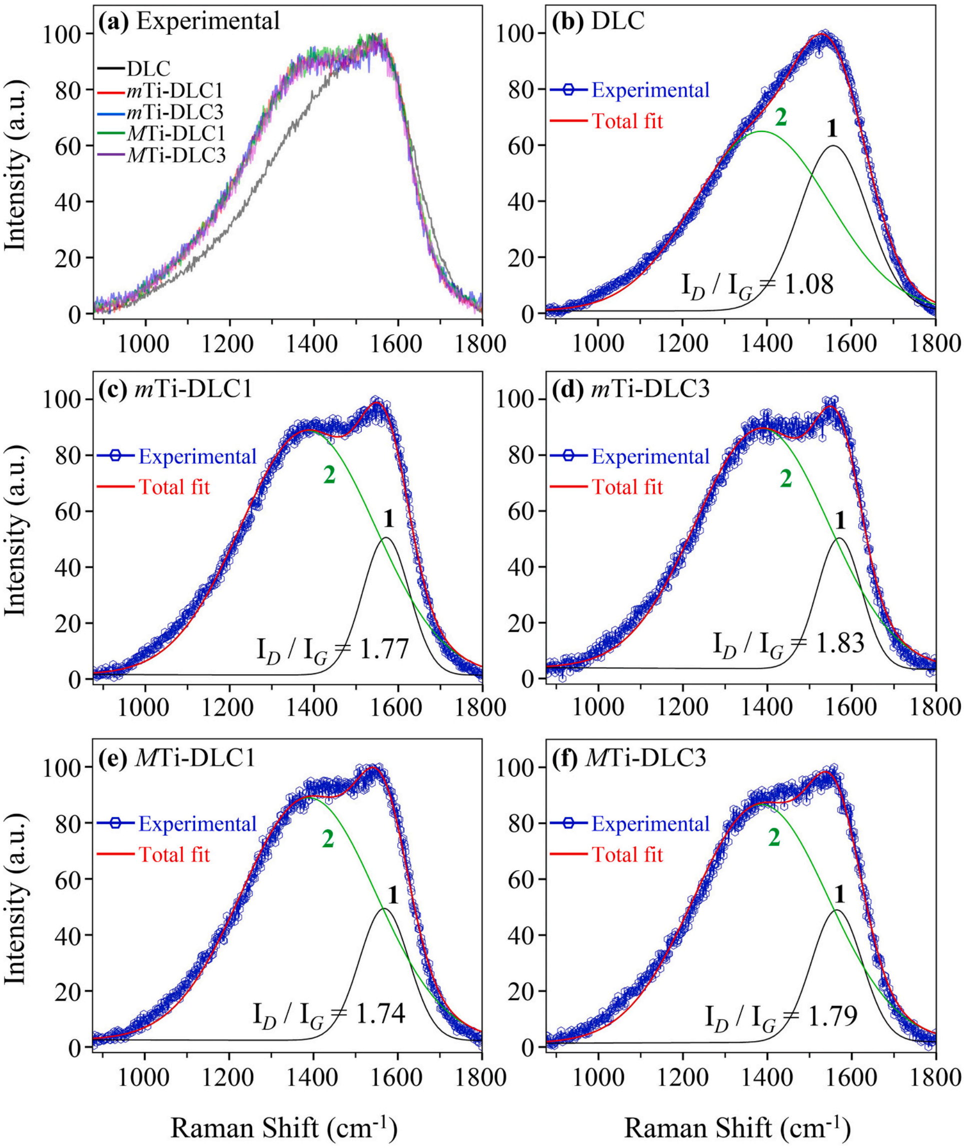

Fig. 3. (a) Normalized and combined Raman analysis results, and peak fitted results for (b) DLC, (c) *m*Ti-DLC1, (d) *m*Ti-DLC3, (e) *M*Ti-DLC1, and (f) *M*Ti-DLC3 coatings.

composition but different periods between consecutive layers of Ti-DLC and DLC (0.4 nm for monolayer and 5.5 nm for multilayer). Despite the identical composition, the multilayer coatings exhibited superior mechanical properties, which were very close to those of undoped DLC.

The uncoated and coated disc specimens used in this work, along with their main properties, are shown in Table 2 [31].

Prior to conducting the tribological tests, the roughness of the steel substrate and the coatings were evaluated using two methods: atomic force microscopy (AFM – Bruker Veeco DiInnova, equipped with a silicon tip having a tip radius of 6 nm, a cantilever frequency of 315–330 kHz, and a data acquisition rate of 0.8 Hz) and white light interferometry (WLI – Bruker NPFLEX 'NPF-12-216').

AISI 52100 steel (DIN 100Cr6 steel) balls from Luis Aparicio Precision Balls, Spain, were used as the counterbodies in the tribological tests. The steel balls had a R_a roughness of approximately 0.04 ± 0.01 µm, measured by a 3D optical profilometer (Bruker - Alicona G4 InfiniteFocus).

2.3. Tribological tests

The tribological tests were performed at room temperature using a tribometer (RTEC-MFT 5000) in a temperature-controlled laboratory at 25 ± 1 °C. The schematic of the tribological testing apparatus is shown in Fig. 1. The tribometer was equipped with a low-temperature drift load cell capable of measuring normal force (F_z), tangential force (F_x), and forces in the Y-direction (F_y). The parameters of interest, primarily the COF (F_x/F_z) was measured by computer-aided software which came with tribometer.

The tests were conducted in a unidirectional ball-on-disc configuration and boundary lubrication regime, with a Hertzian contact pressure of 1 GPa, a normal load of 10 N, a linear speed of 0.55 m/s, and a test duration of 30 minutes, corresponding to a total sliding distance of 990 m, approximately 1 km. These test parameters were chosen to avoid delamination of the coatings during the tribological tests and to allow the additives in the base oil an opportunity to react with the DLC-based coatings as per aim of this research.

Throughout the tests, the ball-to-disc contact was immersed in the oil bath (fully flooded conditions). The total volume of base oil plus additive was approximately 40 ml for each test. The COF values were measured in the steady-state region to obtain reliable readings after a running-in period.

After the completion of the tribological tests, the discs and balls were

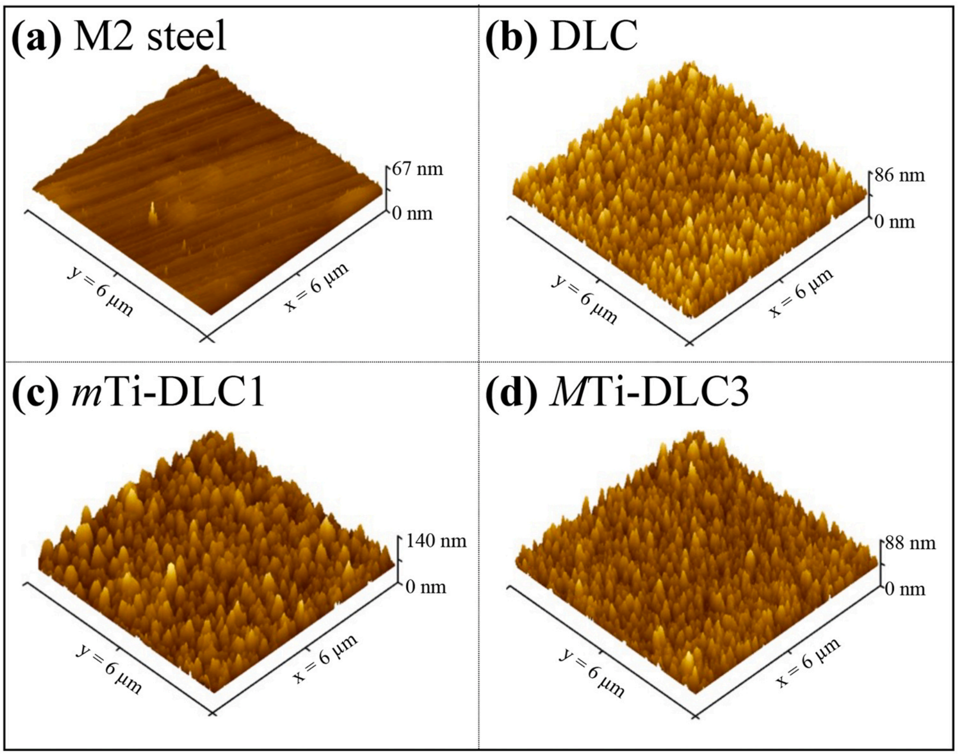

Fig. 4. AFM topographical images for selected samples (a) polished and uncoated M2 steel, (b) DLC, (c) *m*Ti-DLC1, and (d) *M*Ti-DLC3.

rinsed in n-hexane to remove the oil for further analysis, ensuring that the surfaces were not touched by any cleaning media such as wipes, brushes, or foam. The wear volume of both the discs and balls was measured using WLI. The complete procedure is detailed in the supplementary information (SI).

Post tribological test surface of discs and balls were examined using a scanning electron microscope (SEM) (Hitachi-SU3800) for morphological analysis. An energy-dispersive X-ray spectroscope (EDS) (Bruker Nano GmbH – XFlash Detector 610 M) was employed for chemical analysis during the SEM examination. The pre- and post-tribological test surfaces were also analysed using Raman spectroscopy (Renishaw – inVia Raman Microscope). The analysis was conducted at room temperature with a 532 nm wavelength laser, using 5 % laser beam intensity, a 100× magnification of the microscope objective. The exposure time for as deposited coating on AISI M2 steel substrate and for tribologically tested coatings was 15 seconds, whereas exposure time for the wear scar on tribologically tested balls (counterbodies) was 60 seconds.

3. Results and discussion

3.1. Visual stability tests of oil formulations

Before conducting the tribological tests, the stability of the oil formulations was visually inspected at regular intervals of 24 hours, up to a maximum of 384 hours (16 days). No sedimentation, coagulation, or colour change was observed (Fig. 2).

3.2. Raman spectroscopic analysis of coatings

The normalised and peak-fitted results obtained from Raman analysis of the as-deposited coatings, prior to the tribological tests, are shown in Fig. 3. The results are presented for the DLC, *m*Ti-DLC1, *m*Ti-DLC3, *M*Ti-DLC1, and *M*Ti-DLC3 coatings, all of which were deposited on AISI M2 steel substrates.

According to the literature [37], the *D* peak in DLC coatings, which is associated with the breathing mode of sp^2 bonded atoms in ring structures, typically appears in the range of 1300–1450 cm^{-1}. The *G* peak, resulting from the bond stretching of sp^2 bonded atom pairs in rings and chains, generally manifests around 1530–1580 cm^{-1} [37,38]. The ratio between the intensities of these two peaks, commonly denoted as the I_D/I_G ratio, provides crucial information about the extent of graphitisation in the coatings [37]. A higher I_D/I_G ratio indicates greater graphitisation.

As shown in Fig. 3, the undoped DLC exhibited the lowest I_D/I_G ratio, suggesting a lower degree of graphitisation. With the addition of Ti, the Ti-DLC coatings displayed significantly higher I_D/I_G ratios, indicating an increased level of graphitisation, also as reported in [39]. The *m*Ti-DLC coatings exhibited more graphitisation compared to the *M*Ti-DLC coatings, probably due to the higher rotation speed used in the deposition of those coatings.

3.3. Roughness measurements

To calculate the tribological test parameters, the surface roughness of the discs was assessed using two techniques (AFM and WLI) for comparison and validation of the data. Fig. 4 shows AFM representative images of the surface of these samples.

When the roughness measurements obtained by AFM and WLI were normalized for the scan area, the roughness values were identical falling within a few tens of nanometres, specifically ranging from between 9.5 to 17.0 nm of R_q values. The tribological test parameters were derived from the Hamrock-Dowson equation [40,41], which provides a relationship between the geometry of the contact area, the lubrication regime, and the load-carrying capacity of the lubricant.

3.4. COF

The disc samples (uncoated polished steel substrate, DLC, and Ti-doped monolayer and multilayer DLC coatings) were tribologically tested using base oil and oil formulations composed of base oil and additives. Pure base oil and six different oil formulations (as listed in Table 1) were utilised. The measured average COF values are depicted in

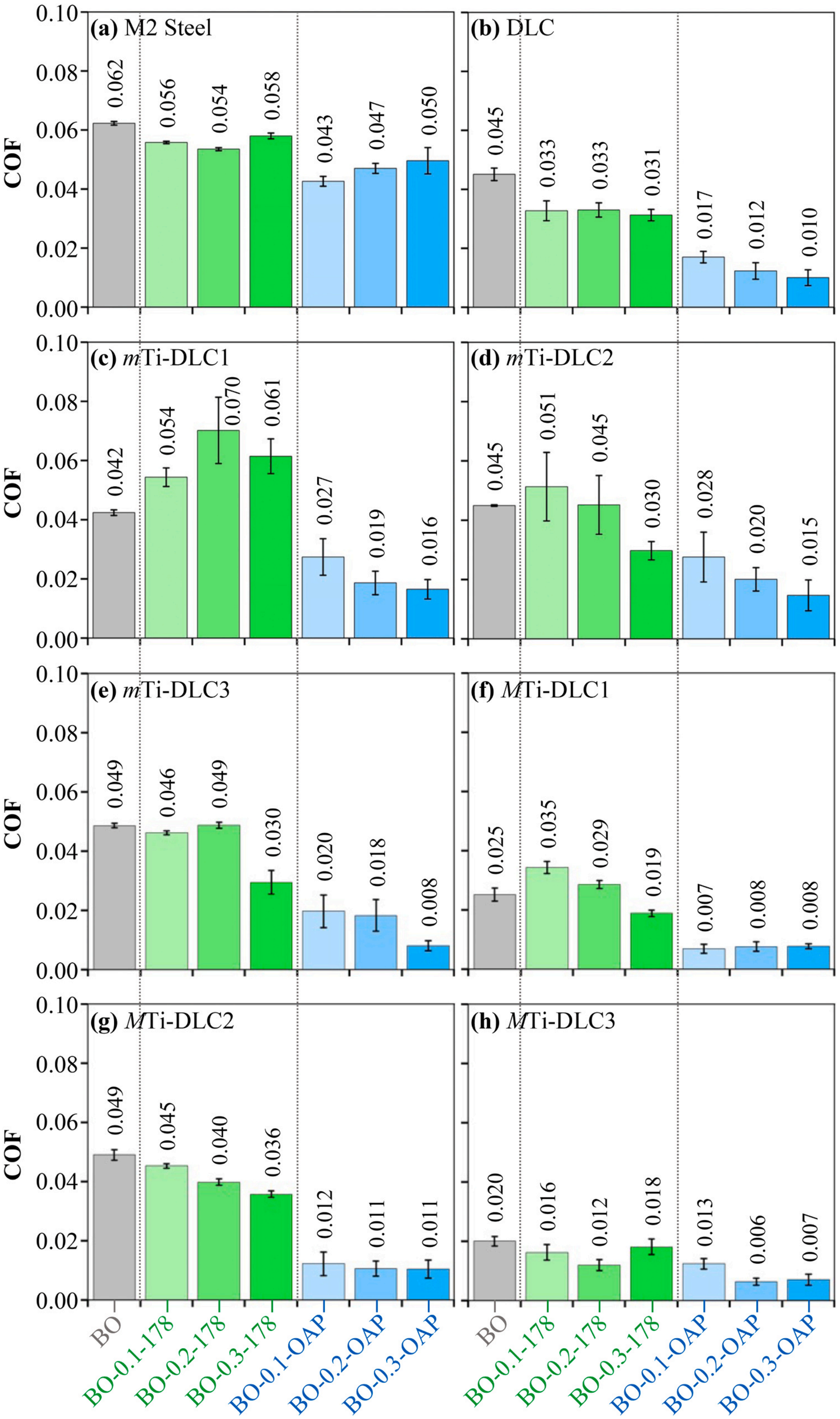

Fig. 5. COF values of (a) M2 steel, (b) DLC, (c) *m*Ti-DLC1, (d) *m*Ti-DLC2, (e) *m*Ti-DLC3, (f) *M*Ti-DLC1, (g) *M*Ti-DLC2, and (h) *M*Ti-DLC3 tested with base oil and all the six oil formulations.

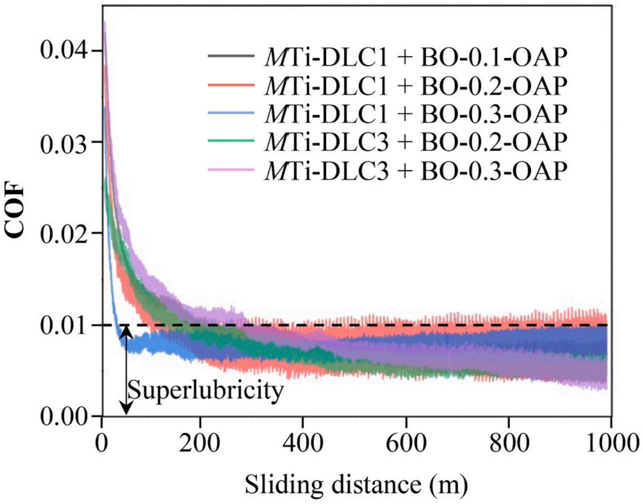

Fig. 6. The COF vs sliding distance curves for the coatings and oil formulation combinations where the superlubricity was achieved.

Fig. 5. Each test was repeated three times, and the COF was calculated after steady-state conditions had been attained. For almost all the tests, steady-state friction was achieved after 200 metres of sliding distance.

The results indicated that for the steel substrate, there was not much difference in the COF values measured for the base oil and the different oil formulations, with values ranging between 0.043 and 0.062. A M Khan et al. [42] reported the same COF values when an AISI M2 steel disc was tested against an AISI 52100 steel counterbody in unformulated PAO4 oil. For the undoped DLC coating, the COF values were lower than those for the M2 substrate. The oil formulations containing the Duraphos® OAP additive resulted in lower COF values than those containing the Duraphos® 178 additive. This trend was consistent across all the Ti-doped coatings. When comparing the monolayer Ti-DLC (*m*Ti-DLC) and multilayer Ti-DLC (*M*Ti-DLC) coatings, the latter exhibited lower COF values. The highest COF value (0.070) was observed for the monolayer coating with the lowest amount of Ti (*m*Ti-DLC1) tested with BO-0.2–178, whereas the lowest COF value (0.006) was obtained for the multilayer coating with the highest amount of Ti (*M*Ti-DLC3) tested with the BO-0.2-OAP oil formulation.

It was possible to achieve superlubricity in multilayer coatings when tested with the oil formulations of BO-OAP. The COF curves for these coatings and oil formulation combinations are shown in the Fig. 6.

It can be seen in the Fig. 6, that steady state friction conditions were achieved after almost 200 m of sliding distance. The presented graphs represent actual data and not the fitted/ smoothened curves. For *M*Ti-DLC1 + BO-0.2-OAP, a broad range of COF was observed, but the average value remained below 0.01. For *M*Ti-DLC3 + BO-0.3-OAP, friction was still decreasing when the tests concluded, indicating that the prolonged tribological tests are required which are aim of the future study.

To understand how the coating's structure (*m*Ti-DLC and *M*Ti-DLC) and the lubricant additive influenced the COF values, Raman analysis was performed on the surfaces of the discs after the tribological tests. The results of this analysis are shown in Fig. 7.

All the coatings shown in Fig. 7(a-f) exhibited increased I_D/I_G ratios compared to the as-deposited coatings. This increase can be attributed to rubbing- or friction-induced graphitisation [43]. Notably, the *M*Ti-DLC coatings showed a substantial rise in I_D/I_G ratios, indicating a higher extent of graphitization, which correlates with the observed lower COF values compared to *m*Ti-DLC coatings. Due to the low concentration of additives in the oil formulation, no signals were detected for phosphorus or phosphorus-derived species. Also, no carbon was detected on the surface of uncoated steel which indicated that the base oil and oil formulations did not deposit a carbon layer on the coatings.

Raman analysis was also conducted on the wear scars on the balls (counterbody), with the non-fitted results displayed in Fig. 8. Curve fitting was not feasible due to the resolution limitations of the curves, which were constrained by the Raman laser intensity and exposure time. These limitations were there due to the delicate nature of the film present on the wear scars.

Contrarily to the wear scars of the balls tested against the uncoated steel, carbon was detected on all the wear scars on the balls tested against the Ti-doped coatings, indicating carbon transfer from the coatings to the balls during the tribological tests. However, the transfer layer was not continuous, likely due to the oil flow. The *D* and *G* bands are visible in the spectra shown in Fig. 8. Although peak fitting was not performed, the prominence of the *D* band shoulder suggests a potentially high I_D/I_G ratio. This increased graphitisation may have enhanced the lubricity of the overall system, contributing to the reduction in COF values.

3.5. *Wear rate*

This study focused on comparing the effects of different oil formulations on the tribological behaviour of DLC coatings, rather than measuring the tribological failure limits of the coatings. As a result of the selected parameters (given in materials and methods), some tests showed wear on the discs that was so minimal to be measurable by the available techniques. The SWR values for the discs and balls are presented in Fig. 9. The WLI images of some discs tested with selected oil formulations, and all the balls tested against BO-0.3-OAP, are shown in Fig. 10.

In Fig. 10(a), wear track images for some selected discs/coatings are presented, obtained by WLI. All the images are 0.45 mm × 0.6 mm in dimensions, with the disc name mentioned in the upper left corner and the oil formulation used in the test mentioned in the upper right corner. The circular arc of the wear tracks can be seen on all the discs, marked by a red rectangle. The depth of the wear tracks was very low, and a depth profile could not be obtained, so the wear volume was measured directly from the WLI scans using the software provided with the WLI equipment. The higher wear of the M2 steel, DLC, and *M*Ti-DLC3 is evident from Fig. 10(a), reflecting the SWR values presented in Fig. 9.

In Fig. 10(b), the wear scars on the balls are shown when tested against all disc samples but only with BO-0.3-OAP. These images were also obtained by WLI. The flat bright circular portion inscribed in the red circle in the middle of the images shows the worn-out part of the balls. The larger was the diameter of the wear scar, the greater was the wear depth, and consequently, the higher was the wear volume. These values were used to calculate the SWR of the balls.

Measurable wear was only present on the discs of M2 steel, DLC, *m*Ti-DLC1, and *M*Ti-DLC3. For the M2 steel, the SWR values varied from 2.06 to 15.8 × 10^{-8} $mm^3N^{-1}m^{-1}$, which is consistent with the literature for steel-steel contacts in PAO4 oil (disc of AISI A2 steel and ball of AISI 52100 steel) [44]. Despite the antiwear nature of both additives, their presence in PAO4 oil resulted in higher SWR values for the steel disc, particularly for the oil formulations containing Duraphos® OAP. Regarding the SWR of the balls, the presence of Duraphos® 178 was beneficial, with SWR values ranging from 0.009 to 0.030 × 10^{-8} $mm^3N^{-1}m^{-1}$, unlike Duraphos® OAP.

When transitioning from the M2 steel disc to the coated discs, it is important to note that the contact conditions differ from steel-steel contacts due to the much higher hardness of DLC-based coatings compared to steel. This may be reflected in the SWR values due to the abrasive action of the gritty surfaces of the coatings. Additionally, these coatings have a granular surface morphology, which can significantly increase the SWR of the balls before steady-state friction is achieved. The undoped DLC showed comparable SWR values to M2 steel, ranging between 2.32 and 11.2 × 10^{-8} $mm^3N^{-1}m^{-1}$, similar to those reported in other studies [45].

Regarding the Ti-doped DLC coatings, measurable wear was only

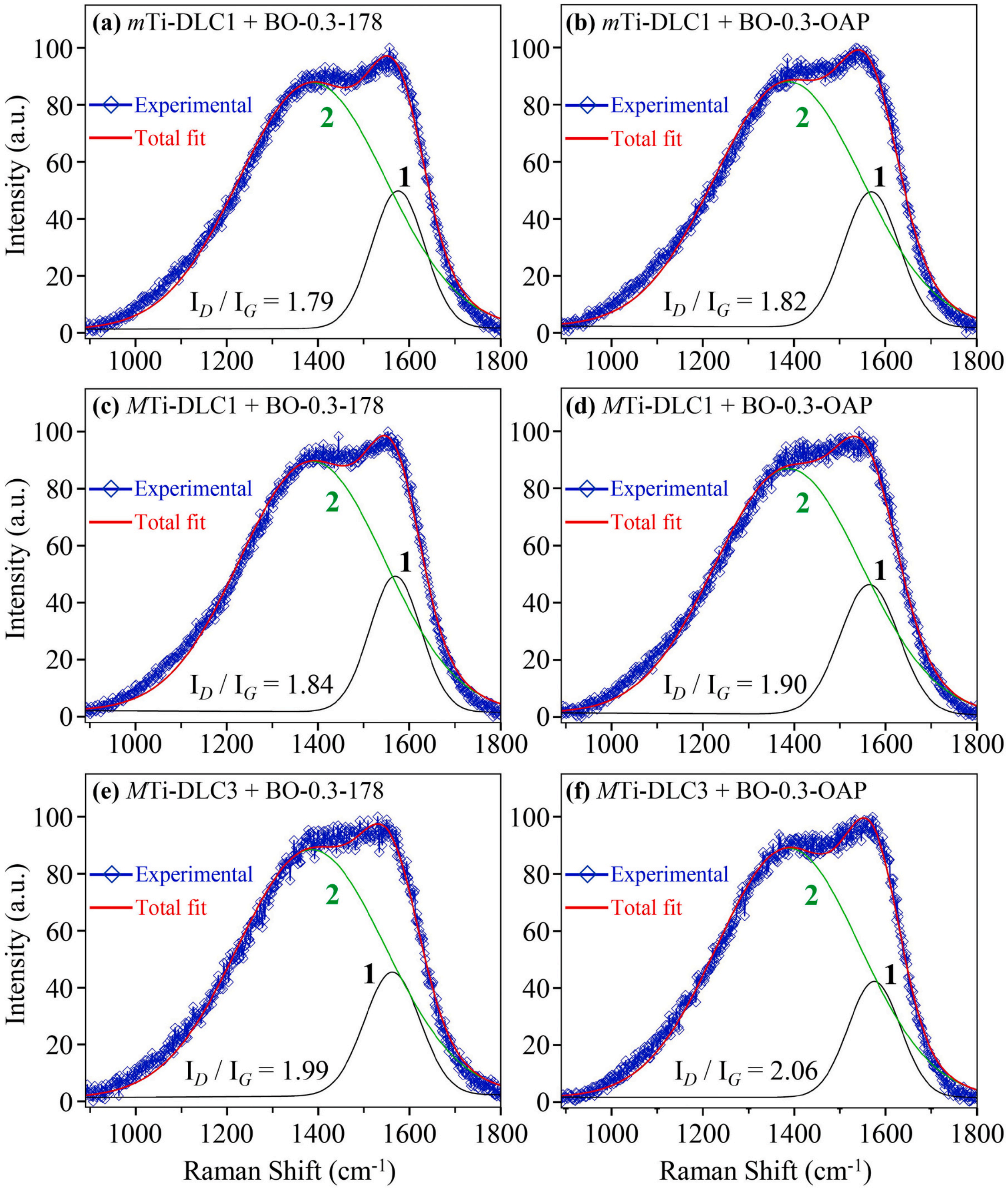

Fig. 7. Raman results for wear track analysis performed on discs after tribological tests (a) *m*Ti-DLC1 + BO-03–178, (b) *m*Ti-DLC1 + BO-0.3-OAP, (c) *M*Ti-DLC1 + BO-0.3–178, (d) *M*Ti-DLC1 + BO+0.3-OAP, (e) *M*Ti-DLC3 + BO-0.3–178, and (f) *M*Ti-DLC3 + BO-0.3-OAP.

observed in samples *m*Ti-DLC1 tested against BO and *M*Ti-DLC3 tested against all formulations except BO-0.3-OAP. The SWR value of *m*Ti-DLC1 tested against BO was 0.43×10^{-8} $mm^3N^{-1}m^{-1}$, which is approximately five times lower than that of M2 steel tested against BO. The multilayer *M*Ti-DLC3 coatings showed measurable wear in the range of 2.01 to 4.53×10^{-8} $mm^3N^{-1}m^{-1}$. Overall, the SWR of the *M*Ti-DLC coatings was higher due to friction-induced softness, as revealed by comparing the I_D/I_G ratios obtained by Raman analysis before and after the tribological tests.

From the results, it can be concluded that the tribological properties (COF and SWR) of the coatings and AISI 52100 balls depended on the chemical composition of the coatings, the distribution of dopants within the coatings (mono- or multilayer structure), the lubricating oil formulations, composition of counterbody, extent of graphitisation in coatings before and after tribological tests, and presence of a lubricious carbon transfer layer from coatings to the balls during tribological tests.

The SWR results were more complex to interpret as compared to the COF. Similar to other studies [42,46], among the Ti-doped coatings, only *M*Ti-DLC3 showed wear, which can be attributed to its lower H, lower E*, lower adhesion with the substrate [31], and higher extent of graphitisation in this coating in result of tribological tests. The wear on the discs was higher for M2 steel and DLC when moving from BO to BO-178 and then to BO-OAP. All the *m*Ti-DLC, *M*Ti-DLC1, and *M*Ti-DLC2 coatings exhibited no detectable wear. Therefore, it can be concluded that the AW+EP additives provided satisfactory results for Ti-doped DLC coatings compared to M2 steel and DLC.

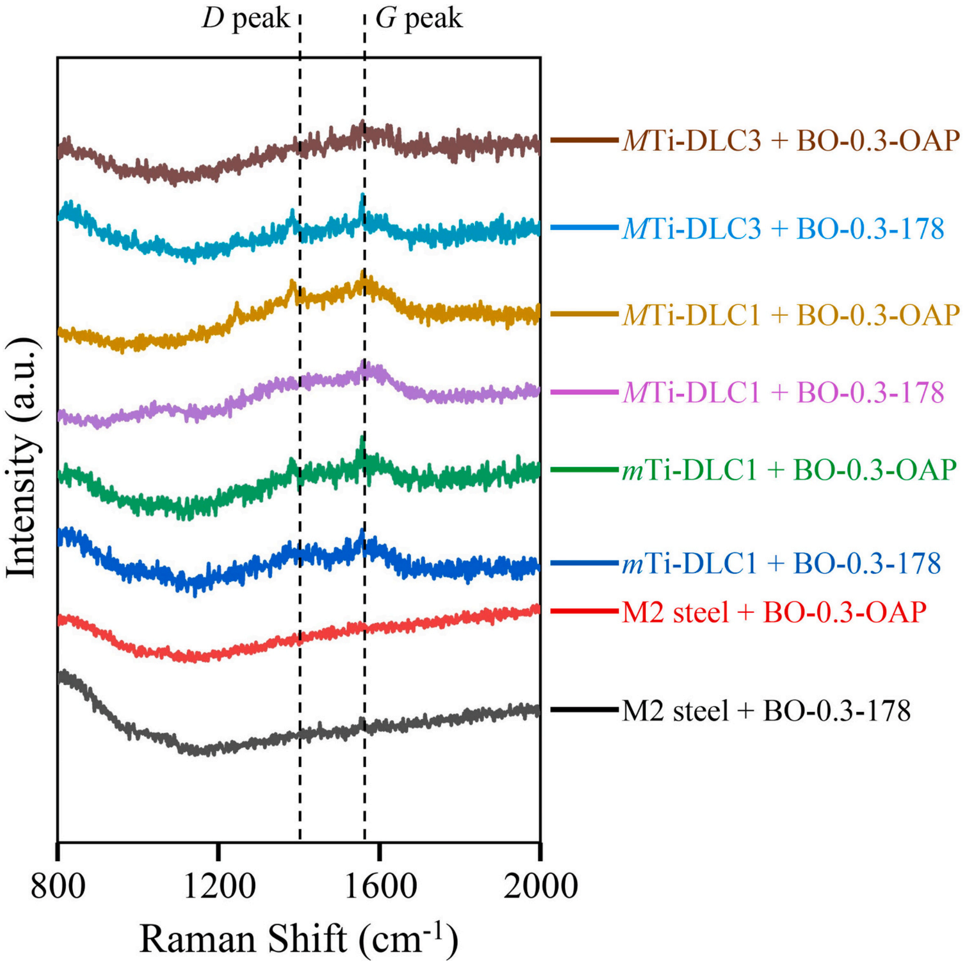

Fig. 8. Raman analysis of the wear scars on the counterbody balls.

To better understand the wear mechanisms of the discs and balls, SEM and EDS analysis was performed to observe the morphology of wear tracks on discs and wear scars on balls, and to quantify the elemental composition of possible tribofilms and potential transfer layers, respectively. The results are shown in Fig. 11 and Table 3.

From the SEM results of the worn-out surfaces, it can be inferred that the coatings did not delaminate from the substrates during the tribological tests. The AISI 52100 steel balls tested against the M2 steel showed scratches and wear marks in the sliding direction with minimal wear compared to those tested against the coated discs (Fig. 11a, b).

The AISI 52100 steel contains approximately 1.1 wt.% (5.6 at.%) carbon and 0.025 wt.% (0.05 at.%) phosphorus in its composition [47]. Given that the additives used also comprised of phosphorus, these composition values served as a basis for observing film composition. Table 3 presents the EDS analysis of the discs and balls for selected tests where either COF or SWR exhibited significantly low or high values, to better understand the wear mechanisms. The EDS sensor was well calibrated to obtain these measurements, as demonstrated in [31], where EDS compositional analysis was compared with results from ERDA-RBS. In Table 3, the name of each disc is provided first, followed by the atomic percentages of phosphorus (P) and carbon (C) detected on both discs and balls when tested with base oil (BO) and oil formulations BO-0.3–178 and BO-0.3-OAP.

Since AISI 52100 steel balls contain approximately 5.6 at.% carbon, it was assumed that if more than 5.6 at.% carbon was detected, it originated from a discontinuous transfer film transferred from the disc to the ball during sliding in the tribological tests. Similarly, with phosphorus, AISI 52100 steel contains approximately 0.05 at.% phosphorus, while DLC and Ti-DLC coatings contain no phosphorus. Thus, if phosphorus was detected at levels exceeding 0.05 at.%, it indicated its originated from the additives. Table 3 contains EDS measurements of phosphorus and carbon for both discs and balls, focusing on the post tribological test surfaces.

It was also observed that wear debris were present on all the discs and balls. EDS analysis indicated that a discontinuous carbon transfer layer was always present on the balls, as the amount of carbon detected was higher than the compositional carbon percentage of the balls. The presence of this carbon transfer layer was also confirmed by the Raman analysis as shown in the Fig. 8. The discontinuity of the transfer layers can be attributed to the high circulation of oil, which removed the wear debris and hindered the formation of a continuous transfer layer, unlike under dry conditions.

Additionally, phosphorus was consistently detected on the discs and balls when BO-178 and BO-OAP oil formulations were used. The amount of phosphorus observed in the EDS analysis was always higher for the BO-OAP oil formulations compared to the BO-178 oil formulations. This observation is due to the composition of the additives (provided in the materials and methods section). The measured values of phosphorus on the discs and balls indicated that there exists a phosphorous based film. The analysis of these possible films by Raman spectroscopy yielded inconclusive results related to phosphorous because of its very low amount in the oil formulations (maximum of 0.3 wt.% of each additive in base oil). The comprehensive analysis of these possible phosphorous containing tribofilm(s) by XPS is the aim of future studies.

While carbon was transferred from the Ti-based DLC coatings to the balls, titanium was not detected in the EDS analysis. This is likely due to

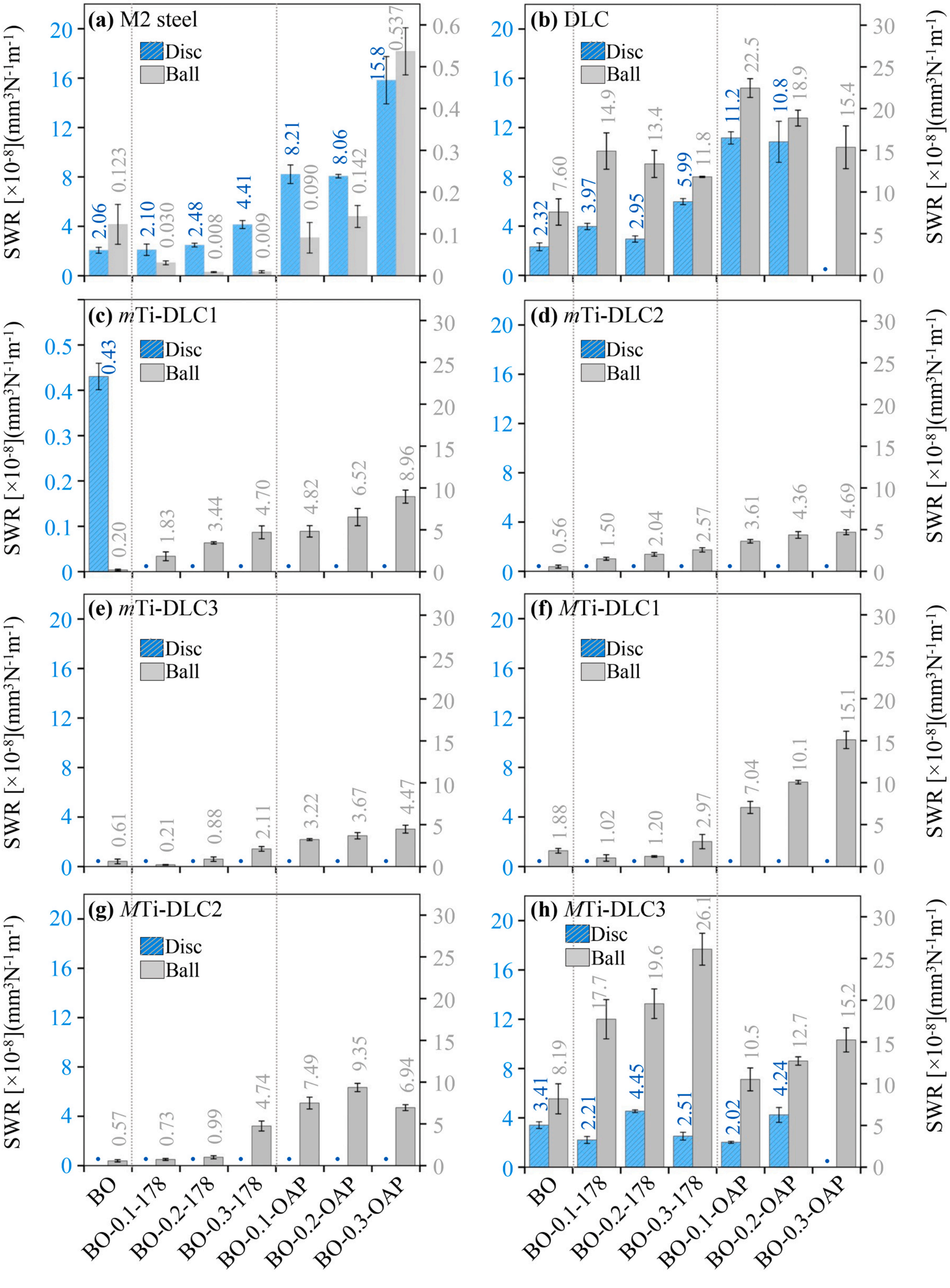

Fig. 9. The SWR of the discs and balls (a) M2 steel, (b) DLC, (c) *m*Ti-DLC1, (d) *m*Ti-DLC2, (e) *m*Ti-DLC3, (f) *M*Ti-DLC1, (g) *M*Ti-DLC2, and (h) *M*Ti-DLC3 against BO and all the oil formulations. The blue dots indicate no observable or measurable wear. The values of disc wear on the Y-axis for *m*Ti-DLC1 and the values of ball wear on the Y-axis for M2 steel are not the same as those in the other plots.

its low concentration of Ti in the coatings and possible leaching during continuous oil flow.

To understand the values of COF, SWR, and the wear mechanism, it is essential to connect the composition and structure of the Ti-doped coatings with that of additives.

The oil formulations of BO-178 showed higher COF values and lower SWR values compared to BO-OAP formulations because it is a phosphate ester with an amine group. The phosphorus reacts with the steel ball to form phosphorous containing films, which help to reduce the SWR of both the balls and discs by reducing plastic deformation [48].

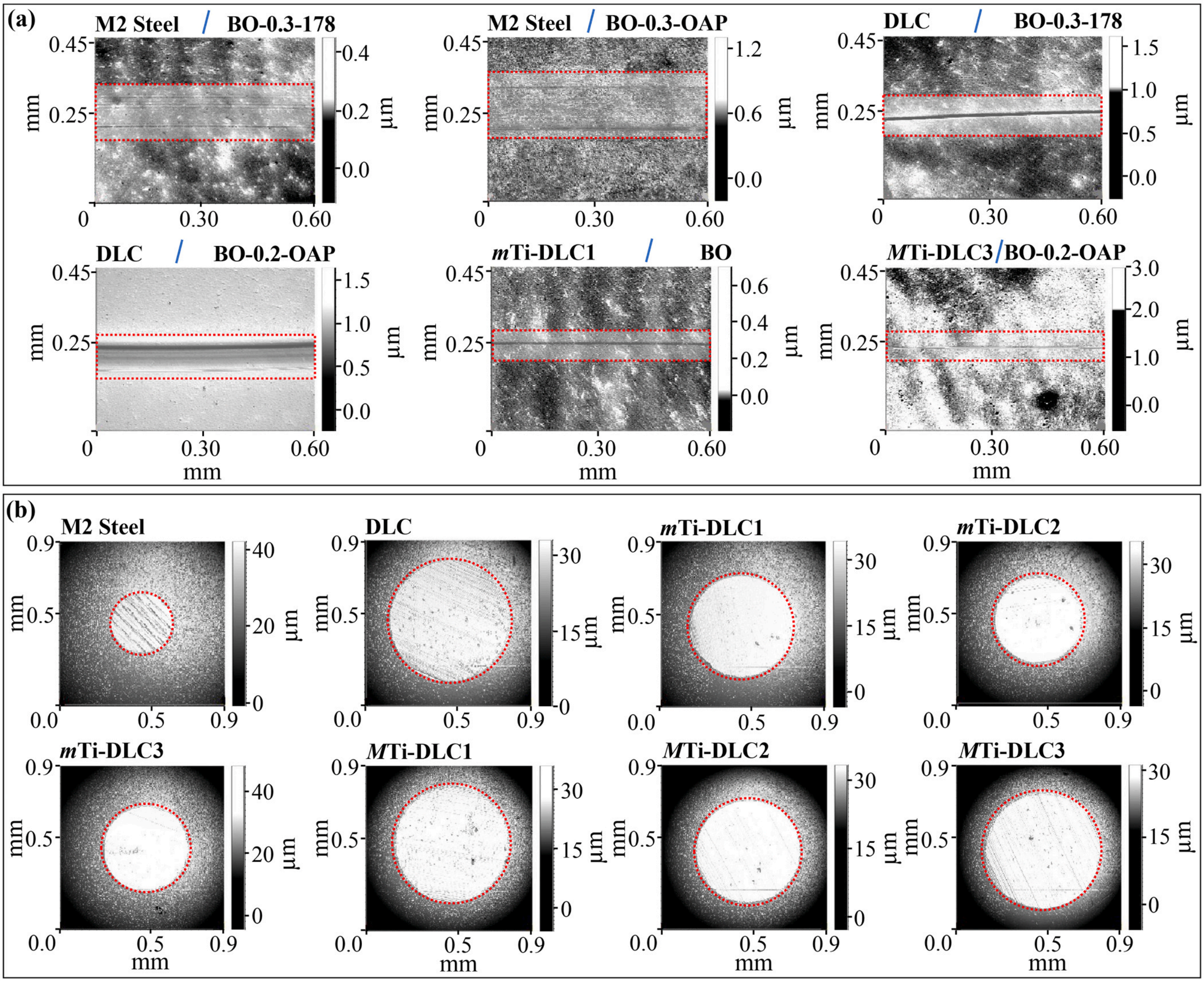

Fig. 10. WLI images (a) wear tracks on selected 'discs + oil formulations', with the disc sample name indicated in the top left corner and the oil formulation in the top right corner of the images, and (b) wear scars on the balls when tested against the BO-0.3-OAP oil formulation to illustrate the wear scar diameter.

Furthermore, the presence of the amine group creates more sites for phosphorous based film formation and enhances the stability of these films [29,30].

For the Ti-DLC discs, it is reported that Ti forms a P-O-Ti covalent bond on the surface of discs when Ti is present and it reacts with phosphorous containing additives. This bond inhibits harsh contact between the disc and the ball, helping to reduce both COF and SWR [26]. The amount of these P-O-Ti bonds depends on the amount of phosphorus in the additive and Ti dopant in the coatings, which is why BO-178 formulations reduce COF less effectively than BO-OAP formulations, but significantly reduce SWR due to the presence of phosphorus and the amine group in a single chemical structure.

The formulations of BO-OAP showed lower COF and higher SWR values compared to BO-178 oil formulations due to the higher phosphorus content, which can form more phosphorous containing films, as evident from Table 3, resulting in a reduced COF [27,28]. Additionally, the BO-OAP oil formulations increased the I_D/I_G ratios more prominently compared to the BO-178 oil formulations, which more effectively reduced the COF, noticeably in *M*Ti-DLC coatings. The SWR values were higher with the BO-OAP formulation because it does not contain an amine group for stabilisation of the possible phosphorus containing film. Additionally, the lower COF is attributed to the higher phosphorus content in this additive, resulting in more P-O-Ti bonds on the surface [26].

The *M*Ti-DLC coatings exhibited the lowest COF values, likely due to the distribution of Ti in these coatings. Although the overall Ti concentration in these coatings was 2.9, 5.9, and 8.9 at.%, the concentration in the Ti-rich layers of these coatings was 15, 32, and 44 at.% [31]. As a synergistic result, the BO-OAP oil formulations provided more phosphorus, and the Ti-rich layers in the *M*Ti-DLC coatings provided more titanium, allowing for the formation of more P-O-Ti bonds, which explains the lower COF values along with more friction induced graphitisation in the coatings. It can be stated that the multilayer structure of the Ti-doped DLC coatings not only improves the mechanical properties but also significantly reduces the COF. The multilayer Ti-doped DLC coatings exhibited superlubricity with selected coatings and oil formulations, as illustrated in the Fig. 6, a result which was not achievable with monolayer Ti-doped DLC coatings.

From the careful analysis of the wear tracks and scars using WLI and SEM, combined with EDS analysis performed after the completion of the tribological tests, the wear mechanism can be defined as shown schematically in Fig. 12. At the start of the tests, the discs and balls began to rub against each other, providing the energy needed to activate the additives. The additives reacted with the balls, forming a phosphorous

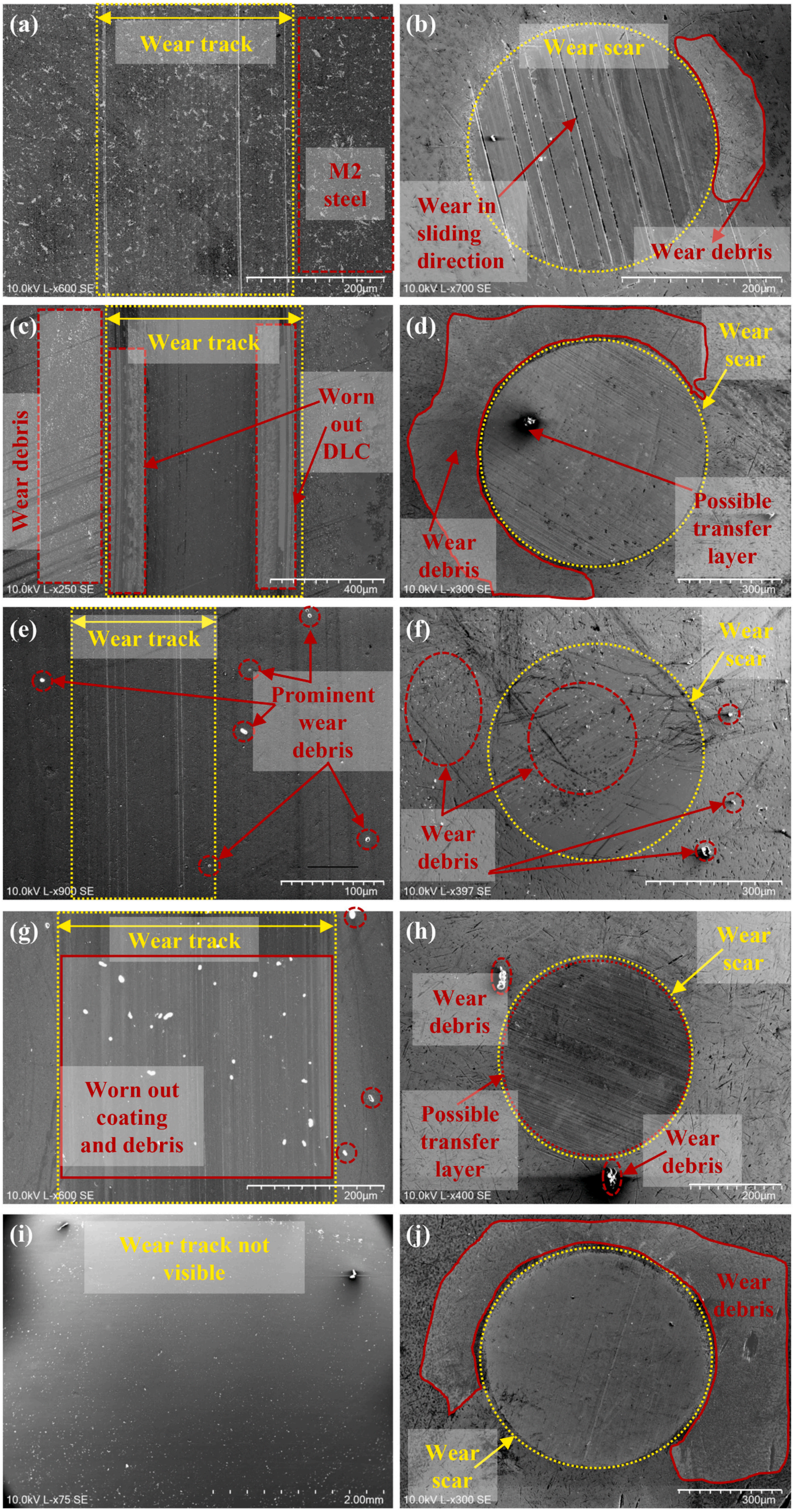

Fig. 11. SEM micrographs of post-tribological surfaces: (left) discs, (right) balls. (a, b) M2 steel + BO-0.3-OAP, (c, d) DLC + BO-0.3-OAP, (e, f) *m*Ti-DLC1 + BO-0.3–178, (g, h) *M*Ti-DLC1 + BO-0.3–178, and (i, j) *M*Ti-DLC3 + BO-0.3-OAP.

Table 3

EDS analysis of the worn-out surfaces: P = phosphorus and C = carbon.

Coating	**M2 steel**			**DLC**		
Oil	**BO**	**BO-0.3-178**	**BO-0.3-OAP**	**BO**	**BO-0.3-178**	**BO-0.3-OAP**
at.% of P ball	-	0.2	0.2	-	-	-
at.% of P disc	-	0.4	2.1	-	-	0.5
at.% of C ball	5.7	10.8	11.5	16.4	23.8	10.0
at.% of C disc	8.1	10.2	13.5	96.2	96.3	92.2
Coating	***m*Ti-DLC1**			***M*Ti-DLC1**		
Oil	**BO**	BO−0.3−178	BO−0.3-OAP	**BO**	BO−0.3−178	BO−0.3-OAP
at.% of P ball	-	1.8	-	-	0.8	0.6
at.% of P disc	-	-	-	-	-	-
at.% of C ball	10.0	10.3	10.7	14.5	11.4	14.8
at.% of C disc	93.8	93.9	93.9	93.6	93.7	93.9
Coating	***M*Ti-DLC3**					
Oil	**BO**	BO−0.3−178	BO−0.3-OAP			
at.% of P ball	-	0.39	0.45			
at.% of P disc	-	0.49	0.49			
at.% of C ball	10.2	11.8	13.6			
at.% of C disc	88.6	88.6	88.5			

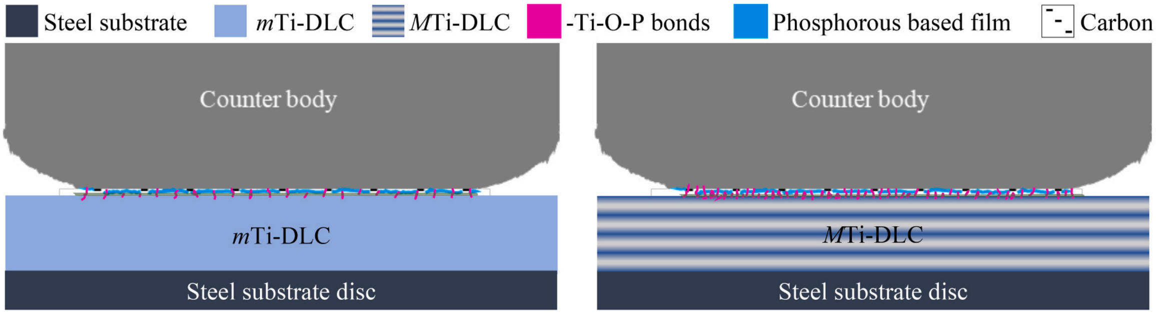

Fig. 12. A schematic of the wear mechanism for *m*Ti-DLC and *M*Ti-DLC coatings.

containing film. This film was more durable with the BO-178 oil formulations due to the presence of both phosphorus and amine groups, thus more effectively reducing SWR values. Although the BO-OAP oil formulations contained more phosphorus to form a film on the counterbody, they lacked amine groups to stabilise the phosphorous containing film, contributing primarily to lowering the COF.

The presence of these phosphorous based films was confirmed by EDS, as shown in Table 3, which measured the phosphorus content on the surface of the wear scars on the balls. A discontinuous carbon transfer film was also present, as confirmed by SEM images and by measuring the carbon content on the balls using EDS along with Raman analysis. For the coated discs of *m*Ti-DLC and *M*Ti-DLC, the Ti in the coatings reacted with the phosphorus in the additives to form a P-O-Ti covalent bond structure on the surface of these coatings. This process depends on the availability of Ti from the coatings and phosphorus from the additives. The multilayer Ti-doped DLC coatings performed better because they contained more Ti in the layers compared to monolayer Ti-doped DLC coatings, and because the multilayer coatings had better mechanical properties. The multilayer coatings also had more graphite like character which helped to reduce the COF reaching in the superlubricity regime.

The wear mechanism is a synergistic effect involving; **(1)** phosphorus-containing species formed on the discs from the reaction of Ti with the phosphorus in the additives, **(2)** the presence of phosphorus-containing species on the balls from the reaction between the alloying elements of the balls and the phosphorus in the additives, and **(3)** friction induced graphitisation in the Ti doped coatings.

4. Conclusions

The tribological properties of newly developed monolayer and multilayer Ti-doped DLC coatings with superior mechanical coatings were successfully assessed against PAO4 base oil containing two different antiwear and extreme pressure additives, namely Duraphos® 178 and Duraphos® OAP. The results were compared to uncoated steel and undoped DLC coatings.

The multilayer Ti-DLC/DLC coatings showed reduced coefficient of friction values achieving superlubricity, reaching as low as 0.006 for the multilayer coating with 8.2 at.% Ti paired with 0.3 wt.% of Duraphos® OAP in the base oil. Measurable wear was only present on the DLC, the monolayer Ti-DLC coating with 2.9 at.% Ti tested with the base oil without additives, and the multilayer Ti-DLC/DLC coatings with 8.2 at.% Ti.

For the wear of balls, the highest values were observed for the balls tested against the undoped DLC coating ($7.60–15.4 \times 10^{-8}$ $mm^3N^{-1}m^{-1}$). Decreased wear was noted for the balls tested against all the monolayer Ti-DLC coatings and the *M*Ti-DLC2 multilayer coating with 5.9 at.% Ti.

Based on the results of white light interferometry, scanning electron microscopy, energy dispersive spectroscopy, mechanical properties, roughness of the samples, along with Raman spectroscopic analysis, it was proposed that wear was reduced in the Ti-doped DLC coatings by the formation of phosphorus containing films on the counterbody and P-O-Ti bonds on the surface of these coatings. A discontinuous carbon transfer layer was present on the balls, and phosphorus was detected when Duraphos® 178 and Duraphos® OAP additives were used. These additives helped to reduce wear and friction in the Ti-doped coatings, with particularly notable results for the multilayer Ti-DLC/DLC coatings. The additives did not perform adequately with uncoated steel and undoped DLC.

In conclusion, the additives explored can be used to reduce wear and friction in multilayer Ti-DLC/DLC coatings while benefiting from their superior mechanical properties and achieving superlubricity. Specifically, the Duraphos® OAP additive can significantly reduce friction, whereas Duraphos® 178 has a prominent effect on reducing wear.

Statement of originality

The submitted research work entitled 'Superlubricity of multilayer titanium doped coatings by using low SAPS organic additives in base oil' for publication in the Journal 'Tribology International', is an original work. The author formulated the research methodology and carried out the research including writing.

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CRediT authorship contribution statement

Ardian Morina: Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition. **Bruno Trindade:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Mobeen Haneef:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Liuquan Yang:** Writing – review & editing, Validation, Supervision, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.triboint.2024.110186.

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