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Wear



Wear control and friction reduction in newly developed multilayer Mg-DLC coatings using organic base oil and sustainable lubrication additives



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ABSTRACT

Two sets of DLC coatings, doped with identical Mg concentrations (6–15 at.%) but exhibiting different monolayer and multilayer microstructures, were deposited via DC magnetron sputtering (DCMS) with varying substrate rotational speeds. The investigation focused mainly on the physical, mechanical, and tribological properties of the coatings. The multilayer coatings demonstrated superior mechanical performance compared to their monolayer counterparts. Specifically, the multilayer coating with 6.1 at.% Mg exhibited a 46 % improvement in reduced modulus and a 26 % increase in hardness compared to monolayer coatings. Furthermore, the multilayer coating with 15 at.% Mg significantly reduced wear on both the disc and ball during testing with a synthetic oil containing an ashless, sulphur-free anti-wear phosphate ester additive with an amine group in its chemical structure.

1. Introduction

Diamond-like carbon (DLC) coatings present self-lubricating properties [1], and excellent abrasion resistance [2], making them highly suitable for applications requiring exceptional wear resistance and low friction. These include tribologically demanding components such as machinery parts, engine components, cutting tools, forming tools, decorative coatings, and biomedical implants [3]. The tribological performance of DLC coatings can be optimised by doping of specific elements [4].

Although DLC coatings possess remarkable hardness and elastic modulus, as well as broad applicability, they are inherently brittle, with low fracture toughness and limited elastic recovery. Additionally, their inert nature restricts reactivity with other chemical species, which can be a limitation in applications where they may hinder the utilisation of such coatings in certain applications where interaction with lubricating oil additives is necessary for minimising wear and friction. One potential solution to address the challenges is the doping of DLC coatings with transition metals. Such doping might reduce internal stresses, improve toughness, enhance thermal stability, and increase the coating's reactivity with beneficial chemical species such as additives in lubricants.

Extensive literature exists on doping of DLC coatings with transition metals, including Ti, Cr, Ni, Cu, Nb, Mo, Ta, W, Au [5], Fe [6], Zn [7], Zr [8], Pd [9], Ag [10], Hf [11], and Pt [12] for various applications and purposes. The dopants mostly utilised in diamond-like carbon (DLC) coatings that exhibit strong carbide-forming tendencies include Ti [13], Cr [14], and W [15]. Titanium has been reported to enhance the mechanical properties of DLC coatings by forming nanometric TiC compound dispersed within the amorphous carbon matrix [13]. Similarly, Cr doping induces the formation of 2-5 nm chromium carbide (CrC) nanocrystals, as verified by XPS and HRTEM [14]. Tungsten is known to form W2C or WC1-x carbides, which contribute to dispersion strengthening and improved wear resistance of the coatings [15]. Conversely, non-carbide-forming dopants investigated in the literature, such as Ag [16] and Al [17] have been reported to facilitate plastic deformation, enhance fracture toughness, and effectively mitigate residual stresses in DLC coatings, outperforming carbide-forming elements in these aspects [16,17]. A similar effect is anticipated with Mg doping in the DLC coatings examined in this study.

In a recent work [18], authors introduced a novel technique for depositing alternating nanometric layers of DLC and Ti-doped DLC using magnetron sputtering. This approach enabled the fabrication of

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nanoscale multilayer coatings with varying titanium concentrations, resulting in enhanced mechanical properties. Further tribological evaluation of these Ti-doped DLC coatings [19] revealed that specific multilayer titanium doped coatings achieved superlubricity when paired with an environmentally friendly lubricant containing an ashless, sulphur-free anti-wear phosphate ester additive, chemically known as 'octyl acid phosphate ($C_8H_{19}O_4P$)'.

Despite the notable properties of transition metals, the s-block elements of the periodic table, particularly the alkaline earth metals, have not been extensively investigated for doping in DLC coatings. Among these, magnesium (Mg) stands out as one of the most significant metals. Magnesium is characterised by properties such as low density, high strength, a moderate melting point, thermal conductivity comparable to aluminium [20], and, notably, biocompatibility and biodegradability [21,22]. These attributes make magnesium suitable for diverse applications, including biomedical implants [23], antibacterial coatings [24], and critical engineering components that require both low weight and high strength. Moreover, the presence of magnesium on surfaces can enhance oleophilicity, promoting more efficient interaction with lubricating oils, which is attributed to Mg's lower electronegativity [25]. These combined properties position Mg as a promising candidate for doping in DLC coatings, making the study of Mg-doped DLC (Mg-DLC) coatings both intriguing and worthwhile. However, there a lack of comprehensive studies on Mg doping in DLC via DC magnetron sputtering, particularly in terms of their mechanical and tribological properties, despite the clear benefits of Mg in demanding applications. Regarding mechanical properties, since Mg is softer than most of the transition metals and is not a strong carbide former, it is anticipated that the mechanical properties might decrease with increasing Mg content. This decrease in mechanical performance is expected to be more prominent as compared to transition metal doping. Additional, due to minimal atomic size difference between C and Mg, reduced internal stresses are expected in the coatings. from a tribological perspective, Mg is known for its solid lubrication properties, which could reduce friction between DLC coatings and the contacting surface, thereby lowering wear rates.

DLC coatings are widely utilised in dry tribological conditions; however, to fully exploit their intrinsic properties, they are frequently paired with lubricating oils [26]. Conventional lubricating oils contain harmful additives such as sulphonated ash, phosphorus, and sulphur (SAPS), in addition to heavy metals like zinc (Zn) and molybdenum (Mo). These traditional oil additives are environmental hazardous, clog catalytic converters, and are not particularly effective in reducing wear on DLC coatings. Therefore, the adoption of organic additives that are SAPS-free and devoid of heavy metals is becoming essential. With the increasing trend of electrification, where a single fluid is used for both lubrication and cooling of electronic systems, issues arise with copper (Cu) in the circuitry being particularly susceptive to corrosion from sulphur in conventional lubricant additives [27]. In response, new additives, typically phosphate esters with an amine group, have been developed. The presence of the amine group in these phosphate esters have been shown to improve the stability of tribofilms [28,29]. Phosphate esters are known to react with ferrous surfaces to form phosphorous-based films, thereby reducing wear and friction [30].

While direct interaction of Mg and phosphorous-containing lubricant additives has not been extensively studied, Mg-based alloys have been evaluated for their interactions with phosphorus-containing species in biomedical applications. Gopi et al. [31] studied the interaction between AZ91 magnesium alloy and phosphate buffered saline (SBF) using immersion methodology. The study confirmed, though EDS and XPS analysis, that Mg interacts with phosphorous at room temperature. Furthermore, Molaei et al. [32] reviewed several Mg-based alloys and their reaction with various electrolytes, including those containing phosphorous -based additives, and confirmed this interaction. A similar conclusion was reached in another study [33]. applications, they demonstrate that Mg can react with phosphorous at the room temperature, potentially forming beneficial films for tribological contacts, such as those in biomedical implants. It is, therefore, expected that DLC containing Mg may also result in the formation of Mgphosphorous by-products.

In the present work, DLC coatings with varying microstructures (monolayer and multilayer) doped with Mg were synthesized. These coatings were characterised in terms of their chemical, structural, and morphological properties, as well as mechanical properties. The tribological performance of the multilayer coatings was evaluated against environmentally friendly lubricating oil formulations containing two additives, both free from sulphur and metals, and exhibiting extremepressure (EP) and anti-wear (AW) properties.

2. Experimental details

2.1. Materials and coating deposition

In this work, two sets of DLC coatings (monolayer and multilayer) doped with Mg were deposited using unbalanced direct current magnetron sputtering (DCMS), following the methodology described in Ref. [18]. The substrate holder was rotating at two distinct angular speeds (1 & 12 rotations per minute) during deposition. The primary objective was to achieve coatings with varying interlayer periods between undoped DLC and Mg-doped DLC, while maintaining a similar elemental composition between the corresponding monolayer and multilayer coatings. At the lower rotational speed of one revolution per minute, coatings with a larger interlayer period were produced, hereafter referred to as multilayer Mg-DLC coatings (*MMg-DLC*). In contrast, at the higher rotational speed of twelve revolutions per minute, coatings with a smaller interlayer period were obtained, hereafter referred as monolayer coatings (*mMg-DLC*).

The coatings were deposited on monocrystalline p-type silicon substrates (100) \pm 0.5° (Siegert Wafer, Germany) and on quenched and tempered AISI M2 steel substrates (Thyssenkrupp Materials Iberica, Spain). The coatings on silicon substrates were analysed for morphological, compositional, structural, and hardness properties, while those deposited on AISI M2 substrates were used for adhesion and tribological testing.

Prior to coating deposition, the steel substrates were first rinsed with a degreaser to remove the rust inhibitor applied by the manufacturer during procurement. The substrates were then ground using a 'Struers Planopol-3' grinding system with planar disc abrasive media up to a 1200 mesh finish. This was followed by polishing using 'Struers MD/DP-Nap' cloth with 6 and 3 μ m μ m diamond-based monocrystalline suspensions. Before deposition, the polished steel samples and pre-cut Si wafers were subjected to ultrasonic cleaning in an Equiultra cleaning bath containing acetone, ethyl alcohol (ethanol), and distilled and deionised water.

A semi-industrial sputtering system, model UDP 650-4, manufactured by TEER Coatings Ltd, was employed for the deposition of the coatings. The equipment was capable of accommodating up to four targets simultaneously. The target set included one 99.95 % pure chromium target, two 99.99 % pure graphite targets, and one modified graphite target with fourteen Mg pellets (purity of 99.99 %) inserted into CNC-machined holes. Each Mg pellet had a thickness of 5 mm and a radius of 10 mm. The two graphite targets were employed for the deposition of DLC layers, whereas the composite target consisting of graphite and Mg pellets was utilised for the synthesis of Mg-doped DLC layers.

The targets were arranged orthogonally with respect to one another, with the configuration of the targets, substrates, and other key components illustrated to scale Fig. 1. The chromium and graphite targets were sourced from PhotonExport, while the Mg pellets were obtained from Testbourne Ltd. The graphite targets had dimensions of 380 mm in length and 175 mm in width.



Fig. 1. Sputtering system according to scale exploded drawing of the sputtering system showing important parts, 'C + Mg' target had 14 Mg pellets embedded in it.

A chromium (Cr) and carbon (C) gradient adhesive interlayer was deposited on the substrates prior to coating deposition. The objective was to enhance adhesion, as DLC coatings inherently exhibit poor adhesion to substrates [34]. Metal-based interlayers improve adhesion primarily by reducing residual stresses [35]. To achieve superior adhesion beyond that of monolithic metal-based interlayers, gradient interlayers are often employed. These interlayers effectively minimize residual stress at the substrate-interlayer interface while simultaneously improving adhesion at the interlayer-DLC coating interface by reducing lattice mismatch and the associated interfacial stresses. The interlayer had an approximate thickness of 0.34 µm, with the carbon concentration varying from 0 % to 100 % across its thickness. At the substrate-interlayer interface, the carbon concentration was 0 %, while at the coating-interlayer interface, it reached 100 %. This gradient structure was achieved by applying 2000 W to the chromium target and negative 50 V bias to the substrate holder for an initial 10-min period. Subsequently, the power applied to the two graphite targets was gradually increased from 0 W to 1750 W, while the power at the chromium target was reduced from 2000 W to 0 W over the next 10 min.

A schematic representation of the two coating microstructures resulting from varying the substrate holder rotational speeds during deposition is shown in Fig. 2. It should be noted that in the *MMg*-DLC coatings, no distinct interface exists between the DLC and Mg-DLC layers due to the rotation of the substrates in front of the targets. Consequently, the term 'period' is used instead of 'layer thickness' to describe the microstructure of the coatings.

Prior to coating deposition, the deposition chamber was evacuated to a base vacuum level of 1×10^{-9} bar. Argon (Ar) was used as the inert gas to generate the plasma required for sputtering. The working pressure during the deposition process was maintained at 1×10^{-6} bar, to ensure clean surfaces for the deposition, the targets were pre-etched to remove surface impurities using Ar plasma at a negative 600 V bias for 15 min before the deposition process began. A shutter system was used to shield the substrates from any unintended deposition during the etching process. Simultaneously, the substrates were cleaned using a pulsed DC bias supply.



Fig. 2. Schematic of the two methodologies used for the deposition of the coatings: (left) monolayer Mg-DLC (*m*Mg-DLC) and (right) multilayer Mg-DLC/DLC (*M*Mg-DLC) coatings.

The parameters for the deposition of coatings and the nomenclature for the coatings used throughout this study are summarised in Table 1. Three types of coatings were deposited: undoped-DLC (one coating), mMg-DLC (monolayer, three coatings), and MMg-DLC (multilayer, three coatings). To achieve three different concentrations of the Mg dopant in the doped DLC coatings, three power settings were applied: 80 W, 135 W, and 200 W for the composite 'C + Mg pellets' target. The choice of power levels was dictated by the minimum threshold required for the given sputtering system to initiate and sustain plasma during the deposition process. Following the determination of the lowest viable power level at 80 W, the additional power values of 135 W and 200 W were selected to facilitate a nearly equi-incremental increase in Mg concentration within the coatings. The power applied to the graphite targets was maintained at 1750 W throughout the deposition. A shorter deposition time was selected for the coatings with high Mg concentrations, as the deposition rate of Mg is significantly higher than that of graphite. This ensured that the coatings had near-identical thicknesses, which also justifies the use of two graphite targets instead of one.

2.2. Microstructure, morphology, composition, and mechanical properties characterisation

The morphology of the coating's surface and cross-section was examined using a field emission electron microscope (FEI-SEM), model Merlin Gemini III, from Hitachi. This equipment was also used for measuring the coating and interlayer thicknesses. Elemental composition was determined using energy dispersive spectroscopy (EDS) with a XFlash Detector 610M from Bruker Nano GmbH. T.

The internal structure of the *M*Mg-DLC coatings was characterised with transmission electron microscope (TEM) using the Titan Themis Cubed 300 from Thermo Fisher Scientific Inc. The EDS tool in the TEM was employed to examine the Mg concentration and distribution within the multilayer coatings, as well as to inspect the elemental distribution within the interlayer. Cross-sectional samples for TEM analysis were prepared using a focused ion beam (FIB) system (FEI Helios G4 CX DualBeam from Thermo Fisher Scientific Inc).

Rutherford Backscattering (RBS) and elastic recoil detection analysis (ERDA) were conducted at the SIAM platform in Belgium to quantify hydrogen and validate the elemental composition obtained by EDS through comparison. The methodology for these techniques is described elsewhere [18].

Structural analysis of the coatings was carried out with x-ray diffraction (XRD) using a X'pert model from Panalytical equipped with a cobalt x-ray tube (k $\alpha = 1.78897$ Å). The analysis was conducted in Bragg-Brentano geometry over a 2 θ range of 30°–60° and in grazing incidence mode to eliminate the effects of interlayer and substrate.

Raman spectroscopic was performed on the pure DLC, *m*Mg-DLC, and *M*Mg-DLC coatings using a Horiba – LabRam HR UV system with λ = 442 nm. data were acquired under standard temperature and pressure (STP) conditions, with three separate acquisition points for each coating, individually each for 15 s. A 100 × magnification objective with a ND1 filter was used.

Hardness (H) and reduced modulus (E^{*}) of the coatings were measured using a nanoindentation test with a NanoTest from Micro Materials Ltd, equipped with a Berkovich indenter. A 5 mN normal load was applied, and tests were conducted in a load-controlled mode, with a 4×4 matrix of indents (16 total per sample) on coatings deposited on Si and AISI M2 steel substrates. The elastic and plastic responses were assessed using H/E^{*} and H³/E^{*2} values [36]. The coatings' resistance to cracking and toughness were evaluated using the energy to fracture (W_e) method, which is directly proportional to the coatings' toughness [37, 38]. These values were calculated using methodology from Refs. [18, 39].

Residual stresses in the coatings were measured using a stylus profilometer (Mitotoyo, Surftest SJ-500) applying the Stoney equation as described in Refs. [18,40].

Adhesion to the substrate was evaluated using a scratch test with a CSEM - Revetest''system equipped with a Rockwell-C scratching indenter. AISI M2 steel substrates were used for this analysis. The test followed ASTM C1626-22 [41], with five scratch passes ranging from 0 N to 50 N, and a 5 mm length per pass, resulting in a loading rate of 10 N/mm. Adhesive failure points (Lc2) were determined on the cracking and delamination observed in optical micrographs obtained using a Leica LH 111 LED microscope.

2.3. Tribological tests

For tribological testing, synthetic PAO4 base oil (polyalphaolefin) from Synfluid – Chevron Phillips Chemicals was used. The oil had a kinematic viscosity \approx 17 cSt at the 40 °C and \approx 4 cSt at 100 °C (1 cSt = 1/100 cm²/s), a density of 0.819 g/cm³, and a CAS number of 68037-01-4.

Two AW and EP additives were included in the oil formulations: Duraphos® 178 (C_{12-14} - alkyl amine isooctyl phosphate) and Duraphos® OAP (octyl dihydrogen phosphate). Duraphos® 178 has the chemical formula ' $C_{19}H_{42}NPO_4 - C_{29}H_{63}NPO_4$ ' and is a phosphorus- and nitrogen-containing ester, comprising 5.95–8.17 wt% phosphorus and 2.69–3.70 wt% nitrogen, with a CAS number of 68187-67-7 [42]. Duraphos® OAP has the chemical formula ' $C_8H_{19}O_4P$ '. As compared to Duraphos® 178, Duraphos® OAP is also an ester containing phosphorus but it lacks the amine group (nitrogen). It is associated with CAS numbers 3991-73-9 and 39407-03-9 [43] and contains 14.73 wt% phosphorus.

Both the PAO4 and additives were provided by TOTAL M&S, Centre de Recherche de Solaize, France. Tribological properties were assessed using pure base oil and three different additive concentrations (0.1, 0.2, and 0.3 wt%) of each additive. The tests were performed on multilayer and undoped coatings, as well as on uncoated AISI M2 substrates. The compositions of the lubricating oil formulations are detailed in Table 2.

An atomic force microscope (AFM), model Veeco DiInnova by Bruker, and with a white light interferometer (WLI), model NPFLEX NPF-12-216 by Bruker were used to assess the surface roughness and topographical features of the tribological test samples.

Tribological tests were conducted using a tribometer, model MFT 5000 by RTEC Instruments, at room temperature in a temperature-

Table 1

Coating's deposition	parameters and	their names to	be used	in this	work
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Sample		Power (W) 'graphite $+$ Mg' target	Power (W) 'graphite targets'	Time (min) for coating's deposition	Rotational speed (rpm) substrate holder
DLC	DLC	0	1750	257	12
mMg-DLC1	Monolayer	80	1750	214	12
mMg-DLC2	Monolayer	135	1750	212	12
mMg-DLC3	Monolayer	200	1750	200	12
MMg-	Multilayer	80	1750	214	1
DLC1					
MMg-	Multilayer	135	1750	212	1
DLC2					
MMg-	Multilayer	200	1750	200	1
DLC3					

Table 2

Oil formulations in PAO4 base oil and their corresponding names to be used in this study.

Additive	Amount of additive in base oil (wt.%)	Oil formulation nomenclature
None	0	во
Duraphos® 178	0.1	BO-0.1-178
Duraphos® 178	0.2	BO-0.2-178
Duraphos® 178	0.3	BO-0.3-178
Duraphos® OAP	0.1	BO-0.1-OAP
Duraphos® OAP	0.2	BO-0.2-OAP
Duraphos® OAP	0.3	BO-0.3-OAP

controlled laboratory environment. The tests were performed under boundary lubrication conditions in a ball-on-disc unidirectional configuration. A 10 mm diameter AISI 52100 steel ball, sourced from Luis Aparicio Precision Balls, Spain, was used as counter body. The average roughness of the steel balls was measured to be $\approx 0.04 \pm 0.01$ μm using an optical profilometer, model Alicona G4 InfiniteFocus by Bruker.

The testing parameters were set as follows: a normal applied load of 10 N, a linear speed of 0.55 m/s, a Hertzian contact pressure of approximately of 1 GPa, and a test duration of 1800 s, corresponding to an estimated sliding distance of \approx 1 km. The counter body to disc contact was submerged in the lubricating oil bath during the tests (flooded conditions). For each test, 40 ml of the lubricating oil formulation was used. An according to scale diagram of the tribometer used in these tests is shown in Fig. 3.



Fig. 3. A scale diagram of the tribometer used in the tribological tests. (a) orthogonal exploded view, (b) assembled cross sectional view with oil flow and oil flow paths, and (c) sample disc orthogonal views with dimensions and an isometric view.

The coefficient of friction (COF) values were directly calculated using the tangential (F_x) and normal (F_z) force sensors in the tribometer, with COF computed as the ratio of F_x/F_z via computer-aided software. After testing, both the counter body balls and the discs were washed with n-hexane to remove oils, preparing them for further analysis.

The wear volume on the counter body balls was measured by capturing micrographs and performing measurements with an optical microscope (same equipment used for scratch adhesion analysis). For the discs, wear volume was measured by WLI (same equipment used for roughness measurements), equipped with Bruker Vision64 Map[™] software for image and data processing. The procedure for wear measurement followed the methodology from Ref. [19].

Following the completion of tribological tests, the morphology of the worn-out surfaces on both the counter body balls and discs were analysed by SEM (SU3800 from Hitachi). For chemical analysis, an EDS equipment (same equipment which was used to analyse coatings) was employed.

3. Results and discussion

3.1. Morphological, compositional, structural and chemical bonding analysis

The morphological characteristics of the deposited coatings were investigated using SEM. To facilitate cross-sectional analysis, the coated Si substrate was cleaved, exposing a freshly prepared fracture surface. The SEM micrographs of DLC, *m*Mg-DLC1, *m*Mg-DLC3, *M*Mg-DLC1, and *M*Mg-DLC3 coatings are presented in Fig. 4.

The interlayer, composed of Cr + C, exhibited an average thickness of approximately $0.34 \mu m$ with a columnar cross-sectional morphology, consistent with prior literature reports [44].

The overall coating thickness ranged between 1.01 and $1.19 \mu m$. Coatings with the lowest Mg content displayed a columnar microstructure as the undoped DLC but with increasingly refined columnar features. Notably, the degree of columnar refinement progressively intensified with increasing Mg incorporation.

Surface morphology analysis revealed a granular, cauliflower-like texture (characteristic of DLC-based coatings) attributable to the atomic shadowing effect [45]. This phenomenon arises due to the preferential oblique deposition of sputtered species onto surface asperities. Furthermore, literature indicates that granule size is influenced by several deposition parameters, including substrate temperature, applied substrate bias, working gas pressure, and incident particle flux [46].

Elemental distribution within the 'Cr + C' interlayer was evaluated via EDS line scans conducted during TEM analysis, as illustrated in Fig. 5 for the *M*Mg-DLC1 coating. The measured interlayer thickness (~0.35 μ m) corroborates the SEM findings. The compositional gradient within the interlayer revealed a chromium-rich region transitioning into a carbon-enriched phase in a non-linear manner. This variation can be attributed to the deposition parameters employed during interlayer synthesis. Specifically, during the initial 10 min, only the Cr target was powered (2000 W), after which its power was progressively reduced to zero over the subsequent 10 min. Concurrently, power supplied to the graphite targets was ramped from 0 to 1750 W. Given the significantly higher sputtering yield of Cr compared to graphite, it is reasonable that substantial compositional changes within the interlayer primarily occurred during the latter stages of deposition when Cr target power was minimal.

The contribution of each target to the coating thickness per substrate revolution was determined based on their respective sputtering rates. The undoped DLC coating was deposited over 257 min with the substrate holder rotating at an angular velocity of 12 rpm, yielding a deposition rate of 4.71 nm/min (equivalent to 0.39 nm per revolution). Carbon deposition in the form of DLC was achieved using two graphite targets operating at equal power, contributing approximately 0.2 nm per target per revolution to the DLC layer formation.

Table 3 shows the thickness of DLC and Mg-DLC (period) per revolution for the DLC, *m*Mg-DLC, and MMg-DLC coatings. Due to varying angular speeds of the substrate holder, the cumulative thickness values differed between the *m*Mg-DLC and *M*Mg-DLC coatings.

The elemental composition obtained by EDS-SEM and RBS-ERDA is shown in Table 4. The compositional values obtained from these two techniques exhibit strong agreement, confirming the proper calibration of the EDS sensor for quantitative analysis. This validation ensures the reliability of all subsequent EDS-derived compositional data. Analysis revealed successful incorporation of Mg into the Mg-DLC coatings at three distinct concentration levels. Notably, the Mg content in the *m*Mg-DLC coatings was nearly identical to that in the *M*Mg-DLC coatings, with only minor variations. These slight discrepancies in Mg concentration are attributed to differences in substrate holder rotation speed during deposition.

The RBS-ERDA analysis detected trace amounts of hydrogen, likely originating from residual water vapour in the vacuum chamber or moisture adsorbed onto the targets prior to deposition. The EDS values shown in Table 4 were measured using a uniform electron beam energy, over an analysed surface area of approximately 5600 μm^2 , at a magnification of 1000 \times . Given that the interaction volume of the electron beam was comparable in both *m*Mg-DLC and *M*Mg-DLC coatings, the observed variations in Mg content can be attributed to differences in layer periodicity. Specifically, the interlayer spacing in *M*Mg-DLC coatings, leading to the slight discrepancies in Mg concentration observed in the EDS data.

Additionally, an extra coating (not shown in Tables 1 and 4) was deposited under the same conditions as *MMg*-DLC3, except that power to both pure graphite targets was disabled, and only the C + Mg target was activated. This deposition was conducted to determine the maximum Mg concentration within the Mg-DLC layers of the *MMg*-DLC coatings. The resulting coating (*MMg*-DLC79), exhibited an Mg content of 78.9 at.% as measured by EDS. Assuming a direct proportional relationship between the power applied to the 'C + Mg' target and the resulting Mg concentration in both *m*Mg-DLC and *MMg*-DLC coatings, the maximum Mg content in the Mg-DLC layers of *MMg*-DLC1 and *MMg*-DLC2 was estimated at 70.0 at.% and 73.9 at.%, respectively. These measured and estimated values are depicted in Fig. 6. Based on these observations, it can be concluded that the Mg content within the multilayer coatings was highest in the central regions of the Mg-DLC layers, while the DLC layers remained entirely devoid of Mg.

Fig. 7 shows the XRD patterns (θ -2 θ mode) of the coatings deposited on silicon substrates. Results for the analysis performed in grazing incidence mode are not shown pictorially as it did not provide any additional information.

The Si substrate exhibited a prominent diffraction peak at $2\theta = 38.60^{\circ}$, corresponding to the (200) plane of a face-centred cubic (fcc) structure, as identified using ICDD reference card #80-0018. The absence of additional peaks associated with Si confirms its monocrystalline nature.

For all coatings, a Cr-related diffraction peak was detected at $2\theta \approx 52.20^{\circ}$, corresponding to the (110) plane of a body-centred cubic (bcc) Cr structure, in agreement with ICDD reference card #85–1336.

The DLC, *m*Mg-DLC, and *M*Mg-DLC coatings did not exhibit any diffraction peaks corresponding to Mg, C, or Mg-C phases, indicating their amorphous structure. This means that Mg atoms are dispersed in the amorphous carbon matrix, in a randomly distributed state. In a study conducted by Kondoh et al. [47] on Mg-C coating deposition by sputtering, it was observed that up to 85 at.% of Mg the coatings were amorphous, and that above this magnesium concentration, the α -Mg phase formed. No magnesium carbide formation was observed. The carbon phase remained amorphous for all the compositions studied. The same result was obtained in this work for the *M*Mg-DLC79 coating, which exhibited a diffraction peak positioned at $2\theta = 39.70^\circ$, corresponding to (002) plane of hexagonal close-packed (hcp) structure of Mg as per ICDD reference card number 01–1141. This result is explained by



Fig. 4. FE-SEM micrographs of the cross-section (left) and surface morphology (right) of the developed coatings: (a, b) DLC, (c, d) *m*Mg-DLC1, (e, f) *m*Mg-DLC3, (g, h) *M*Mg-DLC1, and (i, j) *M*Mg-DLC3.



Fig. 5. TEM-EDS elemental line scan showing the distribution of elements in the 'Cr + C' gradient interlayer, the analysis was performed on the *MMg*-DLC1.

the high concentration of Mg in the *M*Mg-DLC79 coating and confirms the absence of any magnesium carbide formation under the coating production conditions. Same results were obtained when weak carbide-forming metals such as aluminium, copper, or silver were incorporated into DLC coatings [17,48,49].

To confirm these results, the internal structure of the multilayer coatings MMg-DLC1, MMg-DLC2, and MMg-DLC3 was investigated using TEM. The results are presented in Fig. 8, where the period between the layers is denoted by the symbol ' Γ ".

The high-resolution TEM images in Fig. 8 (a, b, c) confirm the presence of a well-defined multilayer architecture within the MMg-DLC coatings. The stratified nature of the coatings becomes increasingly pronounced in samples with higher Mg concentrations and larger interlayer spacings between the DLC and Mg-DLC layers. Minor pinhole defects and waviness observed in Fig. 8 (a, b) are attributed to lamella thinning during focused ion beam (FIB) sample preparation. EDS analysis Fig. 8 (d, e, f) further corroborates the layered structure, highlighting the localised distribution of C and Mg. EDS line scans were performed to quantify the periodicity of the DLC and Mg-DLC layers. However, due to the narrow interlayer spacing, the results for MMg-DLC1 and MMg-DLC2 were inconclusive. For MMg-DLC3, the average interlayer period was determined as 6.1 ± 0.3 nm, based on the EDS line scan Fig. 8 (g). This value closely aligns with the theoretical estimation of 5.5 nm (Table 3), thereby validating previous calculations for coatings with lower Mg content. The observed deviation is likely attributed to the columnar growth morphology, where variations in periodicity occur between the columnar core and the intercolumnar boundaries, as seen in Fig. 4 (SEM analysis).

The SAED patterns in Fig. 8 (a, b, c) further confirm the amorphous nature of the *M*Mg-DLC coatings. The absence of discrete diffraction spots, coupled with the presence of diffuse halo rings, indicates a lack of long-range crystallinity. These findings are in full agreement with the XRD results, reinforcing the conclusion that the coatings remain structurally disordered without the formation of crystalline Mg, C, or Mg-C carbide phases.

Fig. 9 presents the normalised Raman spectra and corresponding peak fitting results for DLC, *m*Mg-DLC1, *m*Mg-DLC2, *M*Mg-DLC1, and *M*Mg-DLC3 coatings.

All the normalised spectra (Fig. 9a) exhibit a broad band within the 900–1800 cm⁻¹ range, which was deconvoluted into *D* and *G* bands using Gaussian fitting functions. As reported in the literature [50], the *D* band (1300–1450 cm⁻¹) is associated with the breathing mode of sp²

Table 3

Depositions rates of Mg-DLC and DLC layers per revolution of substrates.

	Rotational speed of substrates (rpm)	Mg-DLC thickness per revolution (nm)	DLC thickness per revolution (nm)	Total thickness of one rotation
DLC	12	0	0.39	0.39
mMg-DLC1	12	0.01	0.39	0.40
mMg-DLC2	12	0.02	0.39	0.41
mMg-DLC3	12	0.06	0.39	0.45
MMg-DLC1	1	0.27	4.02	4.29
MMg-DLC2	1	0.76	4.02	4.78
MMg-DLC3	1	1.48	4.02	5.50

Table 4

SEM-EDS and ERDA-RBS results for coating's chemical composition. Values indicated by '*' were not measured.

Coating's name	SEM-EDS – atomic %			ERDA-RBS -	ERDA-RBS – atomic %			
	carbon	magnesium	argon	oxygen	carbon	magnesium	argon	hydrogen
DLC.	95.4	0	2.4	2.2	95.3	0	4.0	0.7
mMg-DLC 1	89.9	5.6	2.4	2.1	90.7	6.1	2.5	0.7
mMg-DLC 2	86.0	9.8	3.6	0.6	*	*	*	*
mMg-DLC 3	81.8	14.2	3.3	0.7	82.1	13.9	3.3	0.7
MMg-DLC 1	89.3	6.1	2.8	1.8	*	*	*	*
MMg-DLC 2	85.5	10.0	4.0	0.5	*	*	*	*
MMg-DLC 3	81.2	15.0	3.4	0.4	*	*	*	*



Fig. 6. Distribution of Mg in **(a)** *m*Mg-DLC coatings measured by EDS and **(b)** in *M*Mg-DLC coatings according to experimental and estimated results. Solid lines with markers correspond to the experimental results, and dashed lines correspond to the estimated values based on the EDS results of the coatings.

carbon rings, whereas the *G* band (1530–1580 cm⁻¹) corresponds to the bond stretching of sp² carbon pairs in both rings and chain structure [50, 51]. In agreement with prior studies by Tsai et al. [52] the introduction of a dopant (Ti) in DLC coatings led to a reduction in *G* band intensity. A similar trend is observed in this study, where Mg doping results in a notable decrease in *G* band intensity for both *m*Mg-DLC and *M*Mg-DLC coatings (Fig. 9(b–f)). Additionally, the I_D/I_G ratio in Mg-doped coatings is significantly higher compared to undoped DLC, with a peak shift toward lower wavenumbers. This increase in the I_D/I_G ratio is associated with a greater degree of graphitisation in the coatings [50].

3.2. Mechanical properties

Table 5 presents the mechanical properties, residual stresses and I_D/I_G ratios for the DLC, *m*Mg-DLC, and *M*Mg-DLC coatings.

3.2.1. Hardness, reduced modulus, and residual stresses

The undoped DLC coating exhibited a hardness of 14.26 GPa and a reduced modulus of 167 GPa, consistent with literature findings [53]. The incorporation of Mg led to a reduction in both hardness and reduced



Fig. 7. X-ray diffraction patterns of the Si substrate, 'Cr + C' gradient interlayer, DLC, *m*Mg-DLC, and *M*Mg-DLC coatings (Co K α radiation, θ -2 θ mode).

modulus values in the DLC-based coatings, especially in the case of the monolayer coatings. In these coatings, the hardness values dropped to 9.21 GPa (5.6 at.% Mg), 9.33 GPa (9.8 at.% Mg), and 8.30 GPa (14.2 at. % Mg), while the reduced modulus decreased to 121, 117, and 111 GPa, respectively. For the multilayer coatings, *MMg*-DLC1 (6.1 at.% Mg) exhibited a hardness of 14.56 GPa, surpassing that of pure DLC, 45 % higher when compared to its monolayer counterpart. However, further Mg addition led to a decline in hardness, with *MMg*-DLC2 and *MMg*-DLC3 registering values of 10.08 and 9.88 GPa, respectively.

The reduced modulus values of the multilayer coatings exceeded those of their monolayer counterparts, with percentage improvements of 25.7 %, 23.8 %, and 40.0 % for MMg-DLC1, MMg-DLC2, and MMg-DLC3, respectively. The H/E* and H^3/E^{*2} values followed a similar trend, with MMg-DLC1 displaying the highest values, indicating superior elastic-plastic properties.

The compressive stresses in these coatings arise from the thermal expansion mismatch between the substrate and coatings. Additionally, the residual stresses are influenced by the thickness of the coatings [40]. All coatings in this study displayed compressive stresses, with the exception of the *M*Mg-DLC3 coating.

Table 5 indicates that the mechanical properties of the coatings are directly influenced by the residual stresses. It also shows a dependence on the I_D/I_G ratios: as the I_D/I_G ratio increased, both hardness and reduced modulus values decreased. Zhiquan et al. [54] reported that a higher content of sp³ bonds correlates with increased internal stress, whereas an increasing I_D/I_G ratio indicates a greater presence of sp² sites. In our work, the I_D/I_G ratio increased from 1.62 to 2.09 for *m*Mg-DLC1 to *m*Mg-DLC3, and from 1.56 to 1.91 for *M*Mg-DLC1 to



Fig. 8. TEM analysis of the multilayer MMg-DLC1, MMg-DLC2, and MMg-DLC3 coatings: (a, b, c) high-resolution TEM images and selected area electron diffraction patterns (SAEDPs), (d, e, f) TEM-EDS elemental maps for C and Mg, and (g) Mg intensity along the EDS line scan shown in (f).

MMg-DLC3. According to the criteria outlined in Ref. [54], these results indicated that multilayer coatings retained a higher fraction of sp³ sites after Mg doping compared to monolayer coatings. Consequently, this structural configuration contributed to enhanced both the hardness and reduced modulus. This trend in I_D/I_G ratios affecting hardness and elastic modulus is consistent with observations in Ref. [50].

The internal stresses and I_D/I_G ratios had synergistic effects on these properties. It can also be seen that in the *m*Mg-DLC3 and *M*Mg-DLC3 coatings, the stresses reached almost zero due to the relatively higher amounts of Mg dopant, which acted to relieve the stresses in these coatings. Also, for the same coatings the I_D/I_G ratios were highest amongst the set of coatings studied in this work. For *MMg*-DLC3, the internal stresses changed from compressive to tensile in nature. No reports were found specifically regarding Mg-doped DLC coatings to explain and confirm this observation, but a similar phenomenon was reported for Ti-doped DLC coatings, where a threshold exists for the dopant below which and above internal stresses decrease significantly and abruptly [18,55].

Fig. 10 presents the H^3/E^{*2} and residual stress plots as a function of Mg concentration in the *m*Mg-DLC and *M*Mg-DLC coatings. It was



Fig. 9. (a) Raman normalised results, and peak fitting results of the (b) DLC, (c) *m*Mg-DLC1, (d) *m*Mg-DLC3, (e) *M*Mg-DLC1, and (f) *M*Mg-DLC3coatings. In (b–f) '1' corresponds to position of *G* peak and '2' corresponds to position of *D* peak.

able 5	
Iechanical properties (H, E [*] , W _e , H/E [*] , and H ³ /E ^{*2}), residual stresses, and I_D/I_G ratios from Raman analysis. Values marked by '*' were not measured.	

	Mg (at. %) EDS	H (GPa)	E* (GPa)	W _e (%)	H/E*	$\mathrm{H}^{3}/\mathrm{E}^{\star2}$ (GPa)	Residual stresses (GPa)	I_D/I_G
DLC.	0.0	14.3 ± 1.3	167 ± 8	60.4	0.085	0.103	-0.41 ± 0.15	0.96
mMg-DLC1	5.6	$\textbf{9.2}\pm\textbf{0.8}$	121 ± 6	58.7	0.076	0.053	-0.38 ± 0.16	1.62
mMg-DLC2	9.8	9.3 ± 0.6	117 ± 4	61.5	0.079	0.059	-1.15 ± 0.91	*
mMg-DLC3	14.2	8.3 ± 0.5	111 ± 4	59.7	0.075	0.046	-0.05 ± 0.04	2.09
MMg-DLC1	6.1	14.7 ± 2.0	157 ± 7	67.4	0.093	0.125	-0.79 ± 0.62	1.56
MMg-DLC2	10.0	10.0 ± 1.5	149 ± 9	55.8	0.067	0.046	-0.21 ± 0.29	*
MMg-DLC3	15.0	$\textbf{9.8}\pm\textbf{1.6}$	167 ± 11	53.8	0.059	0.034	$+0.03\pm0.01$	1.91

observed that, in the *M*Mg-DLC coatings, stress consistently decreased with increasing Mg content. However, in the *m*Mg-DLC coatings, stresses decreased as Mg was added to form *m*Mg-DLC1, then increased while moving to *m*Mg-DLC2, and again decreased for *m*Mg-DLC3. The internal stresses and hardness values showed the same trend, indicating that they

were directly related.

The findings indicate that the mechanical properties of the developed coatings are primarily influenced by factors such as the layered structure, Mg dopant concentration, Mg distribution (monolayer or multilayer), and residual stress. In contrast, graphitisation, as reflected



Fig. 10. Residual stress and H^3/E^{*2} of (a) *m*Mg-DLC and (b) *M*Mg-DLC coatings as a function of the Mg concentration.

in I_D/I_G ratios, plays a comparatively minor role. This observation aligns with prior studies on the impact of Ti doping in DLC coatings [18]. The *m*Mg-DLC coatings were deposited at a substrate holder speed of 12 rpm, ensuring a fine distribution of the Mg dopant. The introduction of Mg into the amorphous DLC matrix caused structural distortion due to the slight difference in atomic radii between C and Mg atoms (170 p.m. and 173 p.m., respectively), representing a 1.77 % variance. In *m*Mg-DLC coatings, residual stress values increased in *m*Mg-DLC2 (9.8 at.% Mg) compared to *m*Mg-DLC1 (5.6 at.% Mg), attributed to the higher presence of Mg atoms, as detailed in Table 5. However, when the Mg concentration was further increased from *m*Mg-DLC2 (9.8 at.%) to *m*Mg-DLC3 (14.2 at.% Mg), residual stresses and hardness values both decreased, suggesting that Mg acted as a stress-relieving dopant [56].

For the multilayer MMg-DLC coatings, internal stresses initially increased from -0.41 GPa in the DLC to -0.79 GPa in MMg-DLC1 (6.1 at.% Mg). Subsequently, stresses reduced to -0.21 GPa in MMg-DLC2, and in MMg-DLC3 (15.0 at.% Mg), the stress transitioned from compressive to tensile, registering a value of +0.03 GPa. Among the multilayer coatings, MMg-DLC1 exhibited the highest internal stress levels and the highest values for hardness, reduced modulus, W_e, H/E, and H³/E^{*2}. This elevated stress level, coupled with enhanced W_e, H/E, and H³/E^{*2} values, could contribute to superior resistance against crack initiation and propagation in this coating [57]. Across all Mg-doped DLC coatings, internal stress values showed a direct correlation with hardness, reinforcing the relationship between stress modulation and mechanical properties.

3.2.2. Adhesion

The mean adhesive failure load (Lc2) values, along with their standard deviations (calculated from five measurements per sample) are presented in Table 6.

Representative optical micrographs of the scratch tracks for selected coatings, highlighting the failure points, are shown in Fig. 11 Full-length scratch micrographs are not included, as failure points were not distinctly observable in these images.

The DLC coating exhibited an Lc2 value of 34.0 \pm 4.1 N. All *m*Mg-DLC coatings demonstrated superior adhesion compared to the undoped DLC. Specifically, *m*Mg-DLC1 and *m*Mg-DLC3 exhibited nearly identical adhesion values (47.4 \pm 1.7 N and 48.2 \pm 0.9 N, respectively), while *m*Mg-DLC2 showed a reduced adhesion of 35.8 \pm 7.0 N. This decrease is attributed to elevated internal compressive stresses, as indicated in Table 5.

Table 6Lc2 adhesive failure values for all the coatings.

Coating	Lc2 adhesion (N)
DLC	34.0 ± 4.1
mMg-DLC1	$\textbf{47.4} \pm \textbf{1.7}$
mMg-DLC2	35.8 ± 7.0
mMg-DLC3	48.2 ± 0.9
MMg-DLC1	25.3 ± 1.9
MMg-DLC2	27.0 ± 3.3
MMg-DLC2	47.6 ± 2.3

Scratch morphology analysis of the *m*Mg-DLC coatings revealed a smooth surface with minimal chipping, in contrast to the DLC and *M*Mg-DLC coatings. This improved surface integrity is likely due to Mg doping and the continuous nature of the monolayer coatings. Conversely, multilayer coatings containing Mg concentrations of 6.1 at.% and 10.0 at.% exhibited lower adhesion than both the pure DLC and the mono-layer coatings. The observed reduction in adhesion is associated with high internal compressive stresses, increased hardness (Table 5), and the multilayer structure of these coatings (Figs. 2 and 8). However, the multilayer coating with the highest Mg content (15.0 at.%) exhibited a substantial improvement in adhesion. This enhancement correlates with its lower hardness (9.88 GPa) and the nature of its residual stress. Notably, this was the only coating in the study to exhibit tensile residual stress, whereas all other coatings exhibited compressive stresses.

3.3. Tribological properties

3.3.1. Test samples for tribological tests and roughness measurements

The tribological performance of three multilayer Mg-doped DLC coatings (*M*Mg-DLC) was evaluated, using polished, uncoated AISI M2 steel and undoped DLC coatings as reference samples. The experiments were conducted under lubrication with a base oil as well as six distinct oil formulations (as detailed in Table 2) to assess the interaction of various additive concentrations with the multilayer Mg-doped coatings, each containing a different Mg dopant level.

Surface roughness (R_q) values for the uncoated AISI M2 steel and the coated samples were measured using WLI and AFM to establish the tribological test parameters. This dual-technique approach ensured high-precision roughness characterization. Fig. 12 presents images of selected samples examined using AFM.

For all the coated sample namely DLC, *m*Mg-DLC, and *M*Mg-DLC coatings, R_q values ranging from 4.4 nm–12.7 nm were measured. The roughness values measured by both AFM and WLI were in a nanometric range, and they were consistent with one another when normalised for the scan area.

3.3.2. Coefficient of friction (COF)

Fig. 13 illustrates the coefficient of friction (COF) values measured for the uncoated AISI M2 steel, DLC-coated samples, and *MMg-DLC*coated samples. Each sample underwent three independent tribological tests to determine average COF values and standard deviations. The COF values were recorded once steady-state friction was reached, which occurred at different sliding distances: 300 m for AISI M2 steel, 150 m for DLC, 160 m for *MMg-DLC1*, 200 m for *MMg-DLC2*, and 100 m for *MMg-DLC3*. All COF values presented in Fig. 13 correspond to measurements taken after a sliding distance of 300 m.

Both the undoped and Mg-doped DLC coatings exhibited lower COF values than the uncoated steel. The M2 steel samples displayed the highest COF values, ranging from 0.056 to 0.062, with negligible variation across different lubricant formulations. For all coated samples, the BO-OAP formulations demonstrated superior COF reduction compared to the BO-178 formulations. The lowest COF value (0.017) was achieved with the DLC coating when tested using BO-0.3-OAP. A more comprehensive analysis of the frictional behaviour of these coatings, in conjunction with specific wear rate (SWR), will be provided in section



Fig. 11. Adhesive failure (Lc2) values for selected samples, (a) DLC, (b) mMg-DLC3, and (c) MMg-DLC3 coatings. These values are not average values but associated with the images presented in this figure.



Fig. 12. AFM topographical images of (a) polished AISI M2 steel, (b) DLC, (c) MMg-DLC1, and (d) MMg-DLC3, respectively.

3.3.3.

3.3.3. Specific wear rates (SWR)

Fig. 14 presents the SWR values of the tested balls and discs. Tribological testing was performed under flooded lubrication conditions and within the boundary lubrication regime. Some coatings exhibited negligible wear, which was below the detection threshold of the available measurement techniques, WLI and stylus profilometry. Consequently, only the results obtained via WLI are presented in Fig. 14, while those from stylus profilometry are omitted from this study.

The SWR values for the M2 steel disc ranged from 2.06 to $15.8 \times 10^{-8} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$, consistent with values reported in the literature [58]. All coated disc samples, including the DLC and *M*Mg-DLC coatings, exhibited reduced wear rates compared to the uncoated M2 steel disc, indicating that the coatings, in conjunction with the applied oil formulations, effectively reduced the SWR. Notably, the *M*Mg-DLC coatings, when tested with the BO-178 oil formulation, demonstrated the lowest SWR values, ranging from 0 to $1.79 \times 10^{-8} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$. In contrast, testing with the BO-OAP formulation did not reveal a consistent trend, with the SWR generally higher than that observed with BO-178.

The AISI 52100 steel balls, serving as counter bodies, exhibited a distinct behaviour in terms of SWR, as depicted in Fig. 14. The lowest SWR for the balls was recorded when tested with uncoated M2 steel and

MMg-DLC + BO-178. However, the wear in the latter case approached zero, which contrasted with the former scenario.

3.3.4. Microscopic and compositional analysis of tribologically tested samples

It can also be observed that while BO-178 reduced the SWR, BO-OAP prominently reduced the COF due to the different chemical nature of the additives. To elucidate the mechanisms responsible for the reduction in COF by BO-OAP and the reduction in SWR by BO-178, SEM coupled with EDS analysis was performed on the wear tracks of the discs and the wear scars on the balls, as shown in Fig. 15. SEM and EDS analyses were conducted on multiple samples; however, the results presented here focus on the disc and ball pairs where either the COF or SWR exhibited notable reductions or increases.

The SEM micrographs and EDS analysis indicated that both undoped and doped DLC coatings remained adhered to the substrate, except for *MMg*-DLC3, which exhibited delamination when tested with BO-0.3-OAP (Fig. 15). The AISI 52100 steel balls tested against the polished uncoated M2 steel displayed scratches and wear marks aligned with the direction of sliding. The steel balls tested against DLC-coated discs (both undoped and doped) exhibited more pronounced wear compared to the steel-to-steel contact scenario, with one exception: the *MMg*-DLC3 coating tested with BO-0.3-178 showed no wear, as confirmed by WLI



Fig. 13. COF values for (a) uncoated and polished AISI M2 steel, (b) DLC, (c) MMg-DLC1, (d) MMg-DLC2, and (e) MMg-DLC3 tested with the base oil and all the oil formulations.

and optical microscopy, where wear scars were not visible. However, under SEM with electron contrast, the contact point was still detectable, as shown in Fig. 15h, where it appeared as a dark region of contact without any visible wear.

The counter body steel balls made of AISI 52100 steel composed of AISI 52100 steel, are characterized by approximately 5.6 at.% carbon and 0.05 at.% phosphorus [59]. In comparison, the additive Duraphos® 178 contains about 15 at.% phosphorus, while Duraphos® OAP has approximately 23 at.% phosphorus. These compositions were used as references for investigating the transfer layers and elemental composition of potential tribofilms by EDS analysis. Table 7 summarises the EDS

results for the counter body balls and discs from selected tests. The EDS sensor was rigorously calibrated to ensure accuracy, with results further verified using ERDA and RBS, as detailed in Table 4. In Table 7, each disc's identification is presented first, followed by the atomic percentages (at.%) of carbon (C), phosphorus (P), and nitrogen (N - specifically for Duraphos® 178), as measured on both the discs and the corresponding balls.

Given that AISI 52100 steel balls contain approximately 5.6 at.% carbon, it is assumed that any detected carbon concentrations exceeding this value result from the formation of a discontinuous transfer film from the DLC-coated disc to the ball during sliding. This assumption is



Fig. 14. The SWR of the discs and balls: (a) AISI M2 steel, (b) DLC, (c) MMg-DLC1, (d) MMg-DLC2, and (e) MMg-DLC3 when tested with BO and all the oil formulations. The Y-axis values of disc and ball wear for M2 steel are not the same as those in the other plots (consistent for all other plots). The black and grey dots correspond to samples where the wear was so small that it was not measurable.

supported by the observation that, under conditions of flooded oil lubrication, the transfer layer is less visible compared to dry conditions. Moreover, the counter body balls contain 0.05 at.% phosphorus, while both DLC and Mg-DLC coatings are devoid of phosphorus. Thus, any detected phosphorus levels exceeding 0.05 at.% are attributed to the oil additives. The BO-178 formulations also include nitrogen, which was quantified during the EDS analysis.

Wear debris was observed on the surfaces, with the relative quantity of debris varying across different tests. The carbon content on the balls ranged from 11.8 at.% to 20.9 at.%, significantly surpassing the carbon composition of AISI 52100 steel. This elevated carbon concentration was interpreted as the result of a thin transfer layer originating from the DLC/doped-DLC coatings. Phosphorus was detected on both the discs and balls in association with all oil additives. As presented in Table 7, the phosphorus concentration exceeded that found in the balls, indicating a chemical interaction between the additives and both the counterbody ball and the discs. Additionally, nitrogen was identified when BO-178 oil formulations were utilised in tribological tests, suggesting an interaction of amine groups with the tribological surfaces. Magnesium was also detected on the balls when the disc was coated with an Mg-containing DLC, although this data is not included in Table 7.

The Duraphos® 178 additive is composed of approximately 15 at.% phosphorus in the form of an ester group and 14 at.% nitrogen as part of an amine group, while Duraphos® OAP contains approximately 23 at.% phosphorus as an ester group. The steel counterbody balls interacted with the phosphorus from both additives, leading to the formation of a phosphorus-based layer. This layer contributes to a reduction in the COF and the SWR by minimising plastic deformation of the disc and ball due to its inherent lubricating properties Furthermore, the presence of an amine group is believed to enhance the formation of phosphorus-based films, significantly improving their mechanical and tribological stability [28,29]. This explains the observed reduction in SWR, particularly in formulations containing BO-178 oil, where more stable films were formed due to the amine group. Similar findings were observed in



Fig. 15. SEM micrographs of post tribological test worn out surface: (left) discs wear tracks, (right) ball wear scars. (a, b) M2 steel + BO-0.3-178, (c, d) DLC + BO-0.3-OAP, (e, f) MMg-DLC1 + BO-0.3-178, (g, h) MMg-DLC3 + BO-0.3-178, and (i, j) MMg-DLC3 + BO-0.3-OAP.

Table 7

EDS of worn-out surface. P = phosphorous, C = carbon, N = nitrogen. All the values presented are in atomic %.

· · · · · · ·		
Coating	M2 steel	DLC
Oil	BO-0.3-178	BO-0.3-OAP
P disc	0.6	0.1
P ball	0.2	0.2
C disc	13.3	95.4
C ball	11.8	20.9
N disc	0.1	-
N ball	0.7	-
Coating	MMg-DLC1	MMg-DLC3
Oil	BO-0.3-178	BO-0.3-178
P disc	0.1	0.1
P ball	0.1	0.2
C disc	89.3	81.2
C ball	13.7	16.6
N disc	0.1	0.5
N ball	0.6	0.8
Coating		MMg-DLC3
Oil		BO-0.3-OAP
P disc		0.1
P ball		0.5
C disc		81.2
C ball		18.2

previous studies on multilayer Ti-DLC coatings, where BO-178 oil formulations resulted in the lowest SWR values, which were not measurable [19]. For the BO-OAP oil formulation, more lubricious films were formed, but their mechanical stability was lower due to the higher phosphorus content and the absence of an amine group. These phosphorus-based films exhibit reduced mechanical stability and are more prone to shearing, thereby reducing the COF more effectively than the other additives.

It has been reported that Mg and its alloys form a magnesiumphosphorus-containing film when interacting with phosphoruscontaining additives [60]. Another study demonstrated that such magnesium-phosphorus layers contribute to reduced friction and wear and possess a porous structure that allows them to retain oil for lubrication purposes [61].

In this study, the *M*Mg-DLC3 coatings, which exhibited the highest Mg content, demonstrated negligible SWR for both the counter body balls and discs when tested with BO-178 oil formulations. This indicates that Mg doping can significantly reduce SWR. The reduction in SWR is likely due to the formation of a phosphorus-containing layer on the counter body ball and a magnesium- and phosphorus-containing layer on the disc, in addition to the oleophilic nature of the Mg-doped coatings. Furthermore, the *M*Mg-DLC3 coatings exhibited enhanced graphitisation, as evidenced by their high I_D/I_G ratio, the lowest hardness among the coatings studied, the lowest roughness, and residual stresses approaching zero.

When comparing *MMg*-DLC3 to *MMg*-DLC1 and *MMg*-DLC2, it is evident that wear on both the disc and the ball was more pronounced for the latter two coatings, as they contained lower Mg concentrations. Additionally, *MMg*-DLC1 and *MMg*-DLC2 coatings exhibited higher hardness, increased roughness, and higher residual stress values compared to *MMg*-DLC3.

It can be concluded that BO-178 oil effectively reduced SWR due to the presence of both a phosphate ester group and an amine group. These two functional groups facilitated the formation of a more robust phosphorus-containing layer compared to the one formed by BO-OAP oil formulations. Conversely, the BO-OAP oil formulation was more effective in reducing the COF, as the higher phosphorus content contributed to the formation of phosphorus-containing iron and magnesium layers. However, these layers were less mechanically stable than those formed with BO-178 due to the absence of an amine group.

In addition to the oil formulations and the relative Mg content in the coatings, other properties also played a role in determining the tribological performance. Coatings with higher I_D/I_G ratios exhibited lower SWR for the *M*Mg-DLC coatings. Wear was reduced as internal stresses were minimised. Coatings with higher roughness showed increased wear on both the disc and the ball, while harder coatings induced greater wear on the counter body ball.

4. Conclusions

Monolayer Mg-DLC (*m*Mg-DLC) and multilayer Mg-DLC/DLC (*M*Mg-DLC) coatings with Mg concentrations of approximately 6, 10, and 15 at. % were successfully synthesized using non-reactive direct current magnetron sputtering. The Mg content was controlled by adjusting the rotational speed of the planetary substrate holder to 1 and 12 rpm within the sputtering system. All coatings exhibited a columnar cross-sectional structure and granular surface morphology. The adhesive interlayer and the coatings had identical thicknesses, approximately 0.34 μ m and 1.1 μ m, respectively, ensuring a fair comparison of properties. Approximately 60 % of the interlayer thickness was chromium-rich, while the remaining 40 % exhibited a gradient transition from chromium to carbon.

In the XRD analysis, only a crystalline peak of chromium was detected at a $2\theta = 52.20^{\circ}$, with no peaks corresponding to carbon or magnesium phases. The SAED patterns exhibited halo ring formations without any distinct spots. Both XRD and SAED results confirmed that the coatings were amorphous.

The Raman spectroscopic analysis revealed an I_D/I_G ratio of 0.96 for the DLC coating, while the corresponding ratios for the monolayer and multilayer coatings with the highest Mg concentration (\approx 15 at.%) were 2.09 and 1.91, respectively. The percentage difference between these two Mg-doped coatings was 9 %, indicating that the Mg dopant had a more pronounced effect on the graphitisation of the monolayer coatings.

The most significant adhesion improvements were observed for the monolayer and multilayer coatings doped with the highest Mg concentration (\approx 15 at.%), where adhesion increased by 35 % and 33 %, respectively, compared to the undoped DLC.

All the multilayer coatings exhibited enhanced mechanical properties compared to their monolayer counterparts. Significant improvements in reduced modulus along with hardness were observed for multilayer coatings containing 6.1 at.% Mg, with hardness improving by 46 % and the reduced modulus improving by 26 % compared to the monolayer coating with the same Mg concentration. The hardness for this coating was comparable to that of undoped DLC. Overall, the multilayer coatings exhibited less residual stress compared to monolayer coatings.

Tribological response of multilayer coatings were influenced by the Mg concentration in the coatings, composition of the oil formulations, I_D/I_G ratios, hardness, and roughness of the coatings. These coatings exhibited exceptional low wear, approaching unmeasurable levels compared to both bare steel and undoped DLC. The most significant reduction in wear was observed for the multilayer coating with ≈ 15 at. % Mg (*MMg*-DLC3) when tested with additives containing a phosphate ester with an amine group (Duraphos® 178). These coatings demonstrate strong potential to be used in tribological applications where minimal wear is required, particularly in conjunction with the lubricating oil formulations investigated in this study.

4.1. Future work

- XPS analysis of the coatings to precisely explore the bonding states of Mg and C.
- XPS analysis of the tribologically tested surfaces to analyse the nature of tribofilms formed, helping in formulating a precise wear mechanism for these newly developed coatings.

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- High-temperature tribological tests using the same coatings and lubricating oil formulations to evaluate their performance under elevated temperature oil-lubricated conditions.
- Measurements of the wettability of the coatings to quantify their oleophilicity.

CRediT authorship contribution statement

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

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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.

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Data availability

Data will be made available on request.

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