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The tribological performance of super-hard Ta:C DLC coatings obtained by low-temperature PVD

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ABSTRACT

Diamond-like carbon (DLC) coatings are widely used in industry for decorative/protective purposes or to improve tribological performance in mechanical components. In this study, three types of commercial DLC coatings have been tested and analysed to verify their potential as functional coatings to improve the wear resistance of mechanical components. DLC coatings commercially known as Dianoir, Dropless5000, and Dropless7000 were deposited on AISI 52100 steel through a proprietary cathodic arc physical vapour deposition (PVD) technique, and their properties were compared considering the differences in morphology, thickness, scratch resistance and pin-on-disc test results. The tested coatings showed excellent performance in terms of wear resistance and friction reduction, thereby showing that these coatings may be successfully applied to mechanical components in several applications.

1. Introduction

DLC (diamond-like carbon) is a general term for several metastable amorphous carbon forms. Several researchers [1–4] have shown that the tribological properties of metallic alloys, especially steel, can be improved by applying DLC coatings. DLC coatings are high-performance surface coatings that are based on the special properties of DLC [5]. DLC consists of a disordered mixture of sp^3 and sp^2 bonds, in which the ratio of the sp^2/sp^3 contents affects the properties of the DLC. Since diamond structures are characterised by sp^3 hybridisation, DLC exhibits outstanding mechanical and chemical properties similar to those of diamonds. Accordingly, DLC shows high hardness, chemical inertness, high wear resistance and a low coefficient of friction.

This material family has recently gained increasing importance as coatings because of their promising tribological characteristics; indistinct DLC coatings show exceptionally smooth surfaces, resistance to wear, and low-friction behaviour. They are widely used in several fields, including aerospace, biomedical, food and beverage, and electronics. Zia and Birkett [6] extensively reviewed the background of DLC coatings, including their manufacturing methods, research outcomes, and global revenue over the last decade.

Numerous investigations have been carried out in the tribology field on DLC coatings over the last decade, especially for automotive applications [7–9]. These research activities have pointed out that DLC positively affects the reduction of friction. Moreover, DLC coatings have been tested for applications requiring high-speed motion and low friction, such as rolling bearings [2]. DLC coatings have been successfully applied to ball bearings to improve the frictional interaction between the ball and the raceway [10].

The mechanical and tribological behaviour of DLC coatings depends significantly on the adopted deposition method and the layer composition, i.e., the carbon structure, and doping with elements such as nitrogen, hydrogen, and silicon. These additional elements control the hardness of the resultant film, the level of residual stress, and the tribological properties.

DLC coatings are difficult to produce since the difference between the elastic moduli and coefficients of thermal expansion (CTE) of the metallic substrates and hard films can cause stress concentration at the film-substrate interface or high tensile stress within the films. These stresses can affect the adhesion of the coating to the substrate and thus decrease durability. The strength of the adhesion of the coating to the substrate is an important issue, and it depends on the DLC deposition method. An interesting report on this topic was presented by Ref. [11]. Metallic interlayers are often exploited to improve the adhesion of DLC

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Table 1
Nominal DLC coating properties provided by the manufacturer.

	Dianoir	Dropless5000	Dropless7000
Process	PVD arc	Filtered PVD-Arc	Filtered PVD-Arc
Composition (C:H)	100:0	100:0	100:0
Structure	amorphous	amorphous	amorphous
Sp^3 fraction (%)	70	85	85
Deposition T [° C]	<100	<100	<100
Colour	Anthracite	Black gray	Rainbow
Thickness	1	1	0.5
Density [g/cm^3]	2.8	3.1	3.1
Operating T [°]	500	−80 + 500	−80 + 500
Hardness [GPa]	44	48	68
Hardness [HV 0.05]	4500	5000	7000
Electrical resistivity [μΩm]	10^7–10^9	10^9–10^{11}	10^9–10^{11}

coatings to different substrates, for instance, chrome and tungsten layers. These elements, or, in general, elements belonging to group VI of the periodic table, form strong bonds with the substrates, and metallic bonds reduce the share of covalent bonds. It has also been shown that the surface roughness of the substrate material does not affect the wear resistance of an interlayer [3,11–13].

A variety of techniques have been developed to synthesise diamond-like carbon [14–19]. DLC coatings are generally produced and deposited by means of various physical and chemical methods, such as physical vapour deposition (PVD) and plasma-enhanced chemical vapour deposition (PECVD) processes. However, these two techniques suffer from certain limitations due to the high temperature and required vacuum environment. Moreover, the production volume is limited.

Zia and Birkett [6] conducted an extensive review of the most frequently used DLC deposition methods and the corresponding deposition parameters, such as vacuum pressures, ion energy, substrate preparation, target bias voltage, and target current, which have a marked effect on the structure, growth and properties of DLC.

Among the other methods, filtered cathodic vacuum arc (FCVA) and Plasma Enhanced Chemical Vapour Deposition (PECVD) have shown specific relevant points of strength. FCVA allows better mechanical properties, e.g., elevated hardness, to be obtained (ta-C films); conversely, the PECVD method induces lower mechanical properties because it often results in hydrogenated films (a-C:H films). Consequently, CVD coatings produced using this latter method are also called *soft DLC* [20]. Moreover, the microstructure of DLC can have several variants (amorphous, nano-crystalline, texturised) and be doped with a broad range of metallic, non-metallic, ceramic, or gaseous elements to improve the toughness and wear resistance of the coatings. The elements used for DLC doping can be specifically tailored for specific applications. However, a significant compromise pertaining to the features of DLC is required to boost the specific properties of such coatings, such as corrosion resistance, wear resistance, and thermal stability [21,22].

As reported in literature on DLC coatings [6,23,24], it is possible to deposit hydrogen-free ta-C by using the PVD process, unlike Chemical Vapour Deposition (CVD) or Plasma Enhanced CVD (PECVD), where the resulting coatings always contain hydrogen, i.e., the so-called hydrogenated tetrahedral amorphous carbon (ta-C:H). The process developed

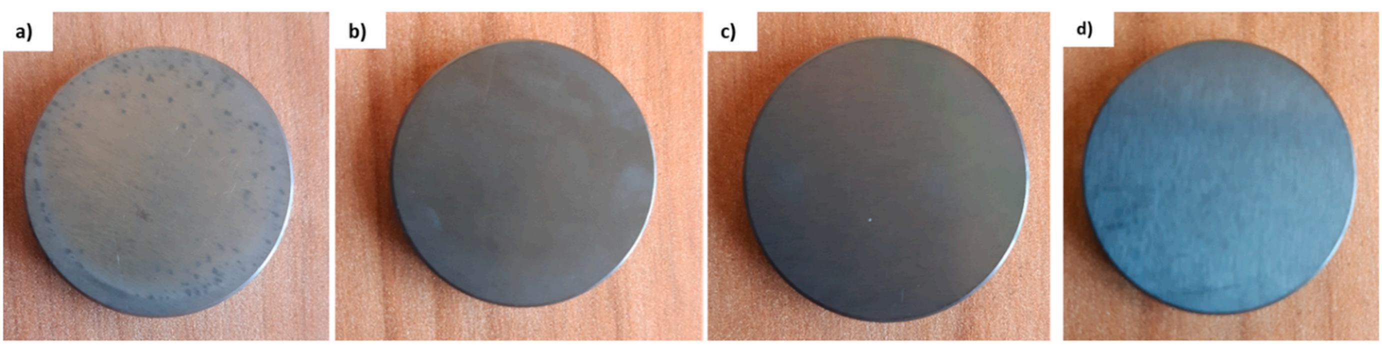

Fig. 1. Bare steel discs used as substrates (a); a ta-C DLC coated sample: (b) Dropless5000, (c) Dropless7000, (d) Dianoir. As a result of the high diamond content, the thin DLC film was transparent and the steel substrate underneath the coating was visible.

Table 2
Test parameters of the pin-on-disc tests. The sampling rate in Friction Test 'B' was increased to maintain the same number of data samples per rotation cycle.

	Load [N]	Speed [m/s]	Duration [m]	Acquisition rate
WEAR TEST	**(ISO 18535)**			
100Cr6	5	0.1	1000	50Hz
FRICTION TEST A	**Variable Load**			
Running-in	5		110	
Load step 1	1		18	
Load step 2	3	0.1	18	50Hz
Load step 3	6		18	
Load step 4	10		18	
Load step 5	15		18	
FRICTION TEST B		**Variable Speed**		
Running-in		0.1	110	50Hz
Speed step 1		0.01	1.8	5Hz
Speed step 2		0.05	9	30Hz
Speed step 3	5	0.15	27	65Hz
Speed step 4		0.3	36	155Hz
Speed step 5		0.5	90	240Hz

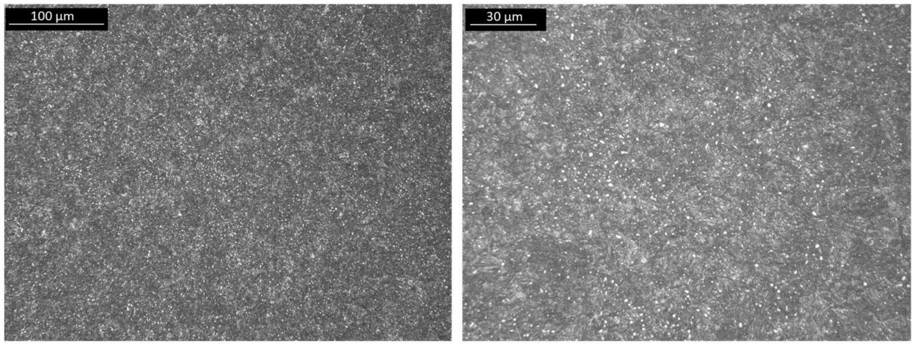

Fig. 2. Nital-etched microstructure of the bare steel (AISI 52100) at different magnifications.

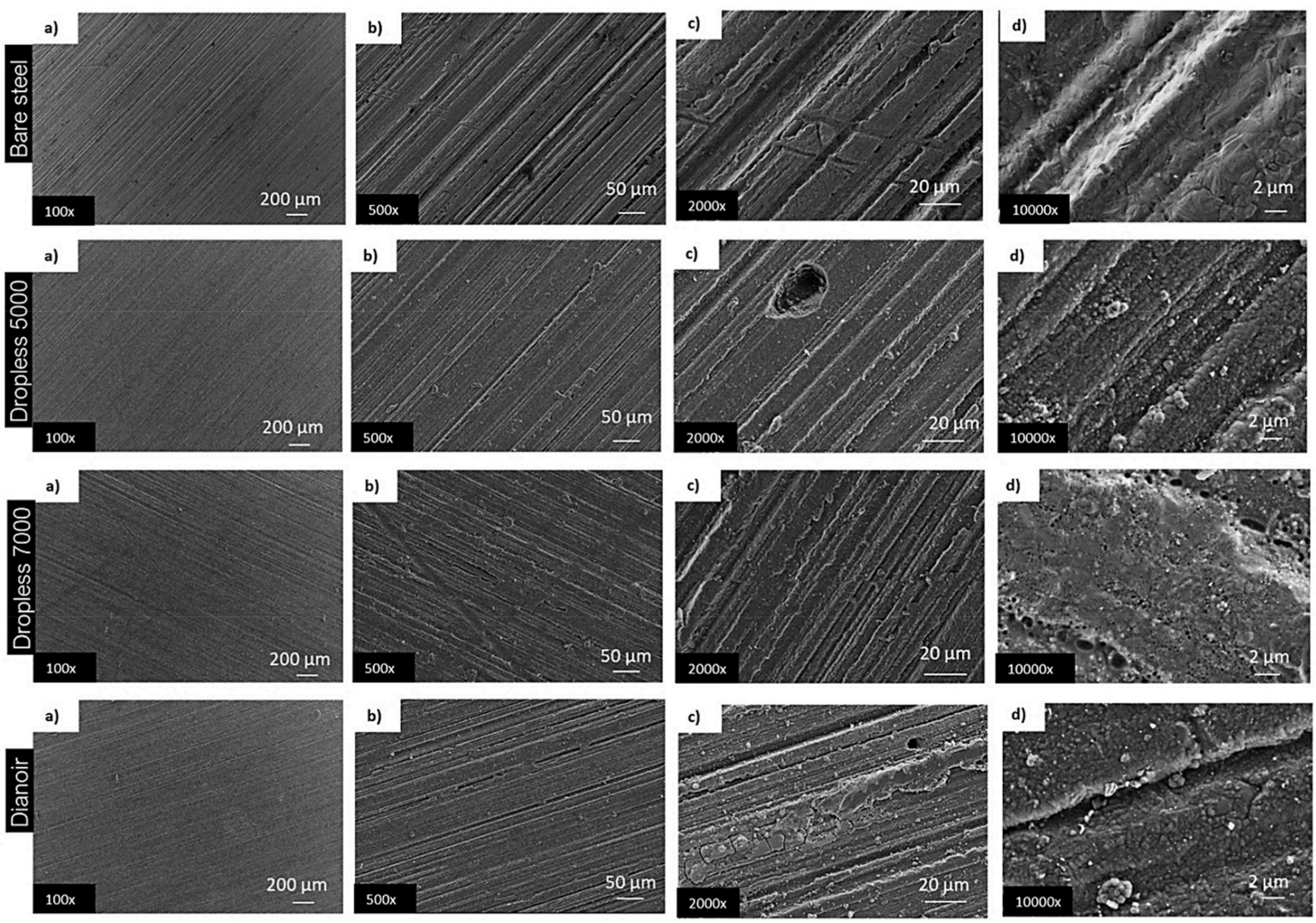

Fig. 3. SEM images of the surface structure of the three DLC coatings compared with the bare steel substrate from low magnification (100 ×) to high magnification (1000×).

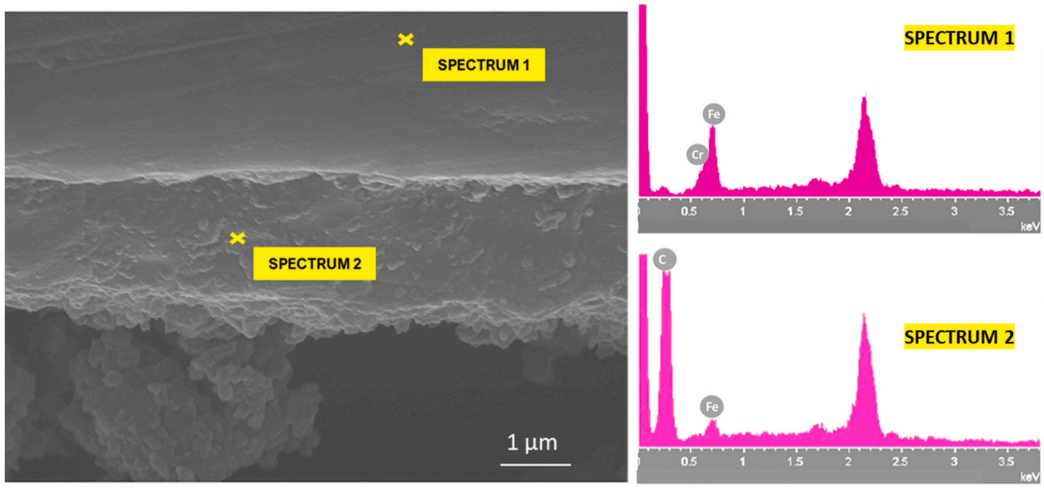

Fig. 4. SEM cross sectional image of a Dianoir 1 µm coating on a steel substrate and the relative EDX analysis results.

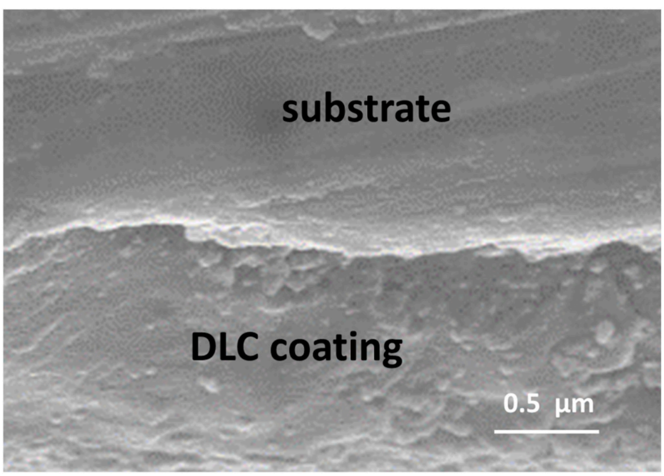

Fig. 5. High SEM magnification of a steel/DLC coating interface.

to deposit the coatings tested in the present work (PVD-Arc) can produce very hard and dense carbon coatings because of the higher sp^3-hybridised carbon bonding content than that of other methods.

Moreover, the filtered PVD-Arc process features easy formation of hard hydrogen-free DLC films that contain more diamond and less graphite because of the high vaporization and ionization rates of graphite [24]. The remaining residual portion is graphite that can be beneficial for improving the gliding properties of the coating.

When DLC is considered as a prospective coating for bearings, it is essential to consider the environmental conditions in which the bearings will work. It has been shown that the friction coefficient can reach low values under vacuum conditions (0.007–0.008), while it may be much higher in humid air (0.20–0.27) [25]. Under vacuum conditions, a high quantity of hydrogen enhances a lower friction coefficient because it induces a certain degree of graphitisation of the DLC coating and prevents the oxidation of the steel surface and DLC. However, this reduce the wear rate of the counterpart but increases the wear rate of the coating [26]. Wu et al. [27] reported that in ambient conditions hard tetrahedral amorhpoud carbon layers feature extremely low friction against steel because of the formation of a third layer of oxides that was

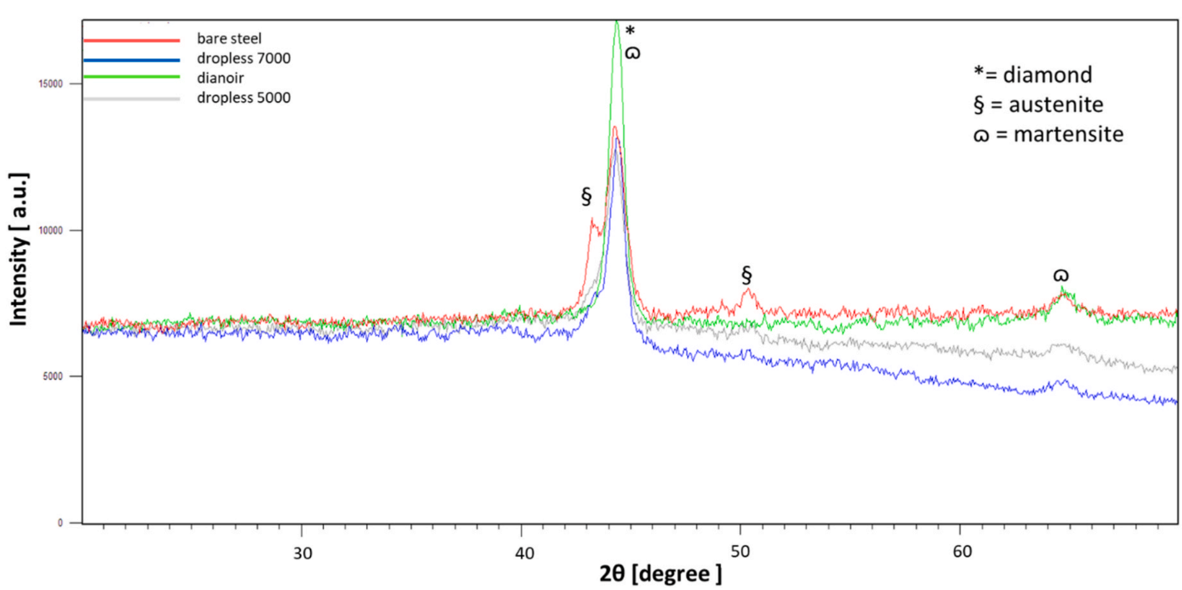

Fig. 6. X-ray diffraction patterns of the DLC coatings and the bare steel.

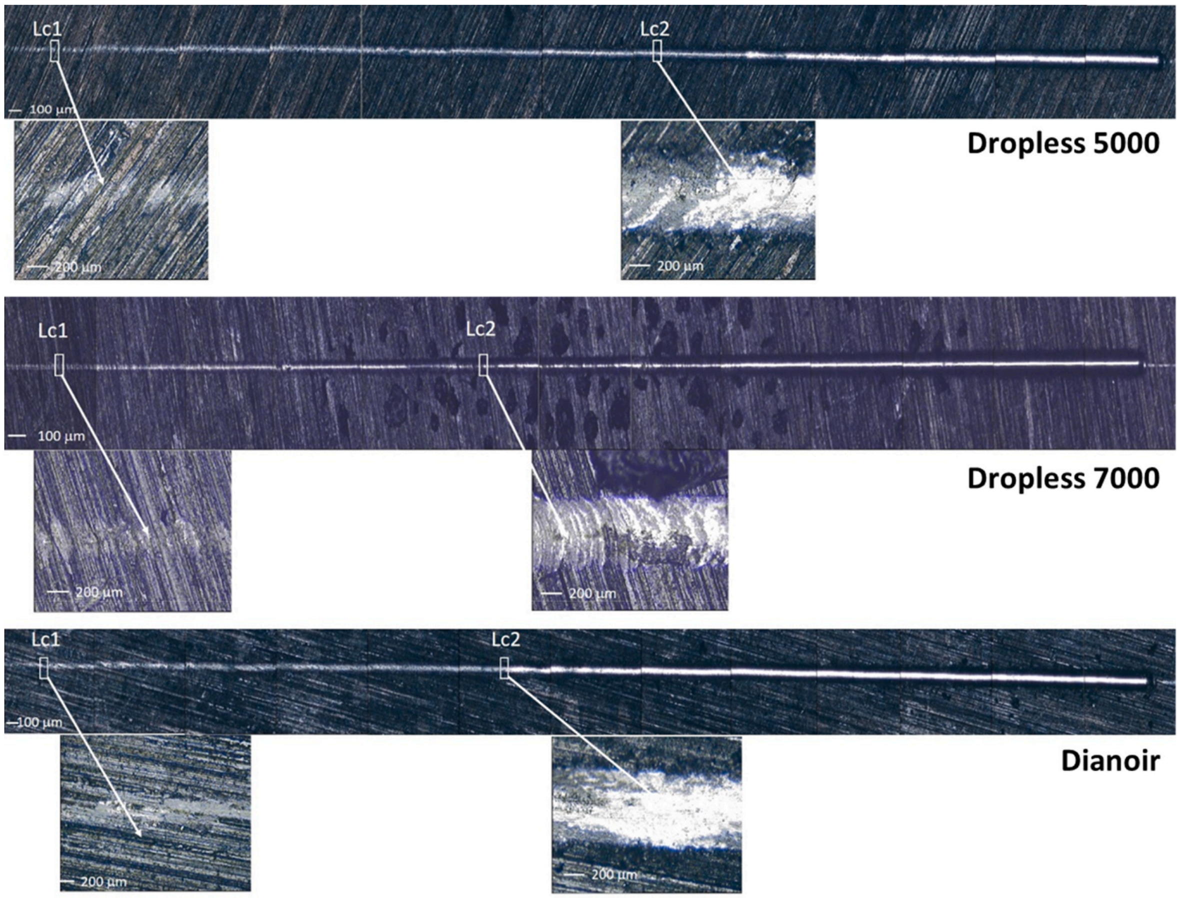

Fig. 7. Optical observation of the scratch track of Dropless 5000, Dropless 7000, and Dianoir.

not present with a-C:H films.

This study compares the performances of innovative super-hard DLC coatings on a rigid steel substrate. The viability of three formulations of ta-C DLC coatings has been assessed to improve friction and wear resistance through morphological analysis, scratch tests, and pin-on-disc testing in the humid air. This paper addresses the tribological behaviour of much harder DLC coatings than those reported in previous research, whose Vickers microhardness reaches up to 7000HV. The aim has been to assess whether these innovative commercial coatings are suitable for application to mechanical components as a functional coating, i.e., cutting tools, bearings, and power transmission mechanisms. Super-hard DLC coatings can offer a technologically and economically feasible alternative to traditional-coated tools for cutting and machining materials. In this paper, the performance of coated and un-coated steel has been explored in order to assess the use of DLC coatings that are traditionally employed for specific components (i.e., decorative applications for watches) for other components, taking advantage of some practical issues, such as surface quality finishing and the expertise of the manufacturer of these coatings in depositing them on complex geometries.

2. Experimental

2.1. Materials and methods

A quenched high-carbon AISI 52100 chrome steel, characterised by a high carbon content (about 1%), was used as the substrate for the DLC coatings. This steel was selected for the study because it is characterised by elevated hardness in the quenched state, a high hardening capacity, high strength, and static fatigue, as well as adequate material durability. It is commonly used for rolling and sliding elements (i.e. rollers, spheres, rings) subjected to continuous movement under high contact pressure.

The AISI 52100 chrome steel was used as received by the supplier, i.e in the quenched and tempered state.

Some discs (diameter 30 mm, thickness 5 mm) were prepared with a surface roughness of Ra = 0.8 μm for the deposition of DLC. The considered DLC materials were all produced by Argor-Aljba SA (CH-6850 Mendrisio, Switzerland, www.argor-aljba.com) and were based on pure carbon [28,29]. The share of the sp^3-configured carbon was around 75–85%, and the discs were certified as hydrogen-free, according to the DLC manufacturing process. The DLC coatings were deposited by means of the “dropless®” technology, that is, a low temperature (<100 °C) PVD arc-filtered deposition process patented by Argor-Aljba SA, which results in homogeneous coverage and coating properties.

Three different types of ta-C (tetra amorphous carbon) DLC were characterised after deposition on steel.

(a) Dropless5000 (coating thickness 1 μm)
(b) Dropless7000 (coating thickness 0.5 μm)
(c) Dianoir (coating thickness 1 μm)

The most relevant properties of these coatings are reported in Table 1 [30].

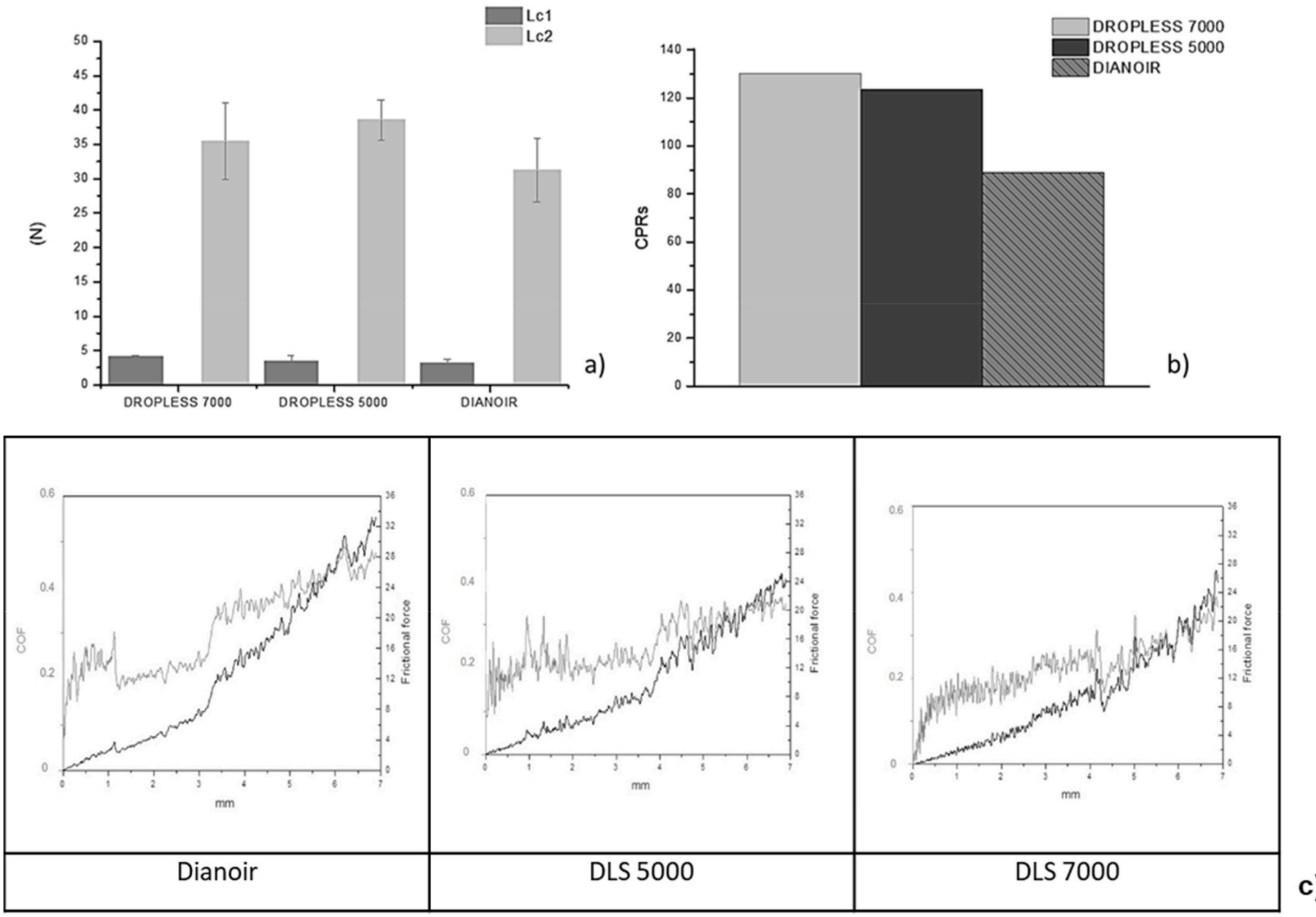

Fig. 8. (a) Critical loads obtained in the scratch test, (b) CPRs, and (c) Friction force and friction coefficient trends.

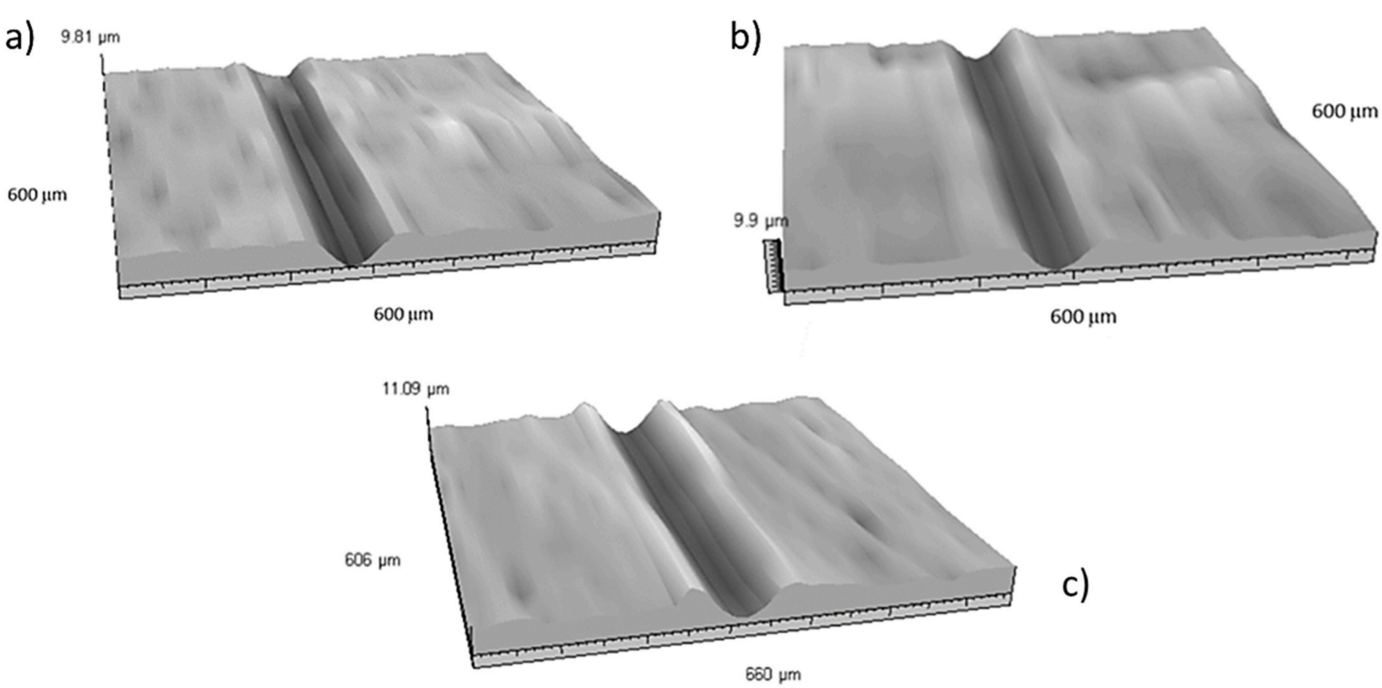

Fig. 9. 3D surface profilometry images (area 600 × 600 μm^2) of (a) Dropless 5000, (b) Dropless 7000, and (c) Dianoir.

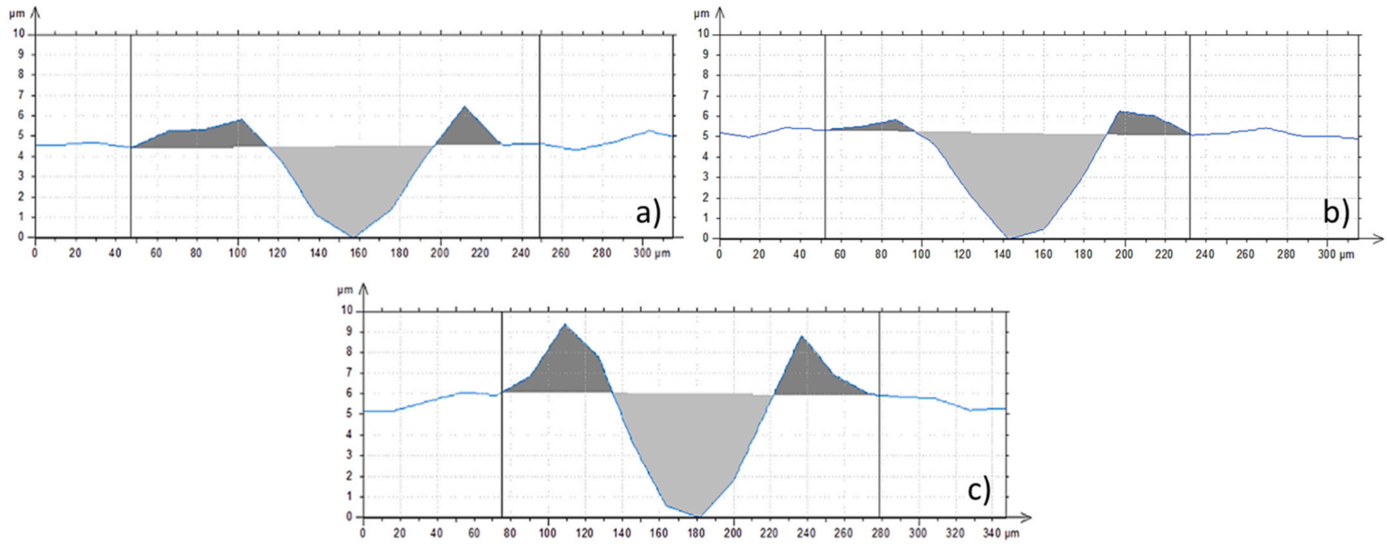

Fig. 10. 2D surface profiles of (a) Dropless 5000, (b) Dropless 7000, and (c) Dianoir.

2.2. Preparation of the samples

Steel discs were cut from cylindrical bars, ground, and then polished to obtain flat and parallel surfaces with a tolerance of 50 μm, and surface roughness of Ra = 0.8 μm. The flat discs were ultrasonically cleaned in acetone to remove any residual liquid and dirt particles. DLC coatings were deposited over the whole surface of the steel discs (Fig. 1).

All the surfaces of the steel discs have been coated with DLC. The discs are kept in a vertical position and rotated during the deposition step, using a specific sample holder; as a consequence, the discs are coated evenly on all exposed external surfaces.

2.3. Surface characterisation

The AISI 52100 chrome steel have been analysed from the morphological point of view.

The steel samples have been submitted to grinding with SiC abrasive papers, followed by polishing with clothes impregnated with diamond paste with grit size of 6, 3 and 1 μm. After the polishing step, the sample were etched with Nital 2% etchant according to standard metallographic procedures. The so prepared samples were observed by light optical microscopy Leica MeF4 type.

Additionally, the morphology of the bare steel and coated samples was investigated, through Scanning Electron Microscopy (QUANTA INSPECT 200, Zeiss SUPRA TM 40), equipped with Energy Dispersive Spectroscopy (EDAX PV 9900). Energy dispersive X-ray spectrometry (EDS) was used to qualitatively detect impurities or chemical elements different from C in the DLC coating.

Samples were not coated with conductive film before morphological observation, in order to avoid potential influences on compositional analysis. Microscopical analyses were performed before and after the tribological tests. The coating structure was investigated by means of X-Ray Diffraction analyses (XRD, PANalytical X'Pert Pro PW 3040160, Philips); the Bragg–Brentano camera geometry and Cu Kα incident radiation were used to investigate the structure of the coatings. Moreover, grazing angle measurements were performed, with an incident angle fixed at 1°, using a parallel beam configuration. An analysis of the patterns was carried out using X'Pert High Score software and the PCPDF data bank.

2.4. Scratch tests

Progressive load scratch tests were performed to evaluate the coating-to-substrate adhesion/cohesion behaviour. The tests were conducted in ambient air, at a temperature of 23 °C, using a CSM scratch tester (Revetest) equipped with a Rockwell diamond indenter and a 200 μm tip radius. The scratch tests were performed at a scratching speed of 10 mm/min and loading rate of 100 N/m, under an initial load of 0.9 N, and final load of 70 N. Three repetitions were carried out for each coating, and an average value of the critical load was thus obtained. An optical microscope, coupled with the scratch test machine, was used to identify the critical loads (Lc) in panorama image mode. Two critical normal loads (Lc1 and Lc2) were used to measure coating adhesion. The critical load, Lc1, occurred at the first failure and corresponded to the initial cracking, while Lc2 corresponded to complete coating delamination. Moreover, the two critical loads were used to calculate the crack propagation resistance (CPRs), according to eq. (1).

$$CPRs = Lc_1 \bullet (Lc_2 - Lc_1) \quad (1)$$

It has been suggested that CPR values can represent the scratch toughness of a coating as they indicate the tendency of scratch cracks to initiate and propagate [31]. A tridimensional surface analysis was conducted using a Form Talysurf 120 profilometer equipped with a conical stylus (tip radius of 2 μm) to acquire the morphology of the scratches. The friction coefficient and the frictional force were continuously recorded during scratching.

2.5. Pin-on-disc tests

Standard tribological tests were performed using a pin-on-disc tribometer (TRB, Anton Paar). The samples coated with the three DLC coatings were tested against a 6 mm AISI 52100 steel ball. Three kinds of tests were performed separately to investigate the frictional and wear behaviour of the coatings. Table 2 provides details on the setup parameters for the tests pertaining to the movement against steel.

Wear tests were performed as per the ISO18535:2018 standard to

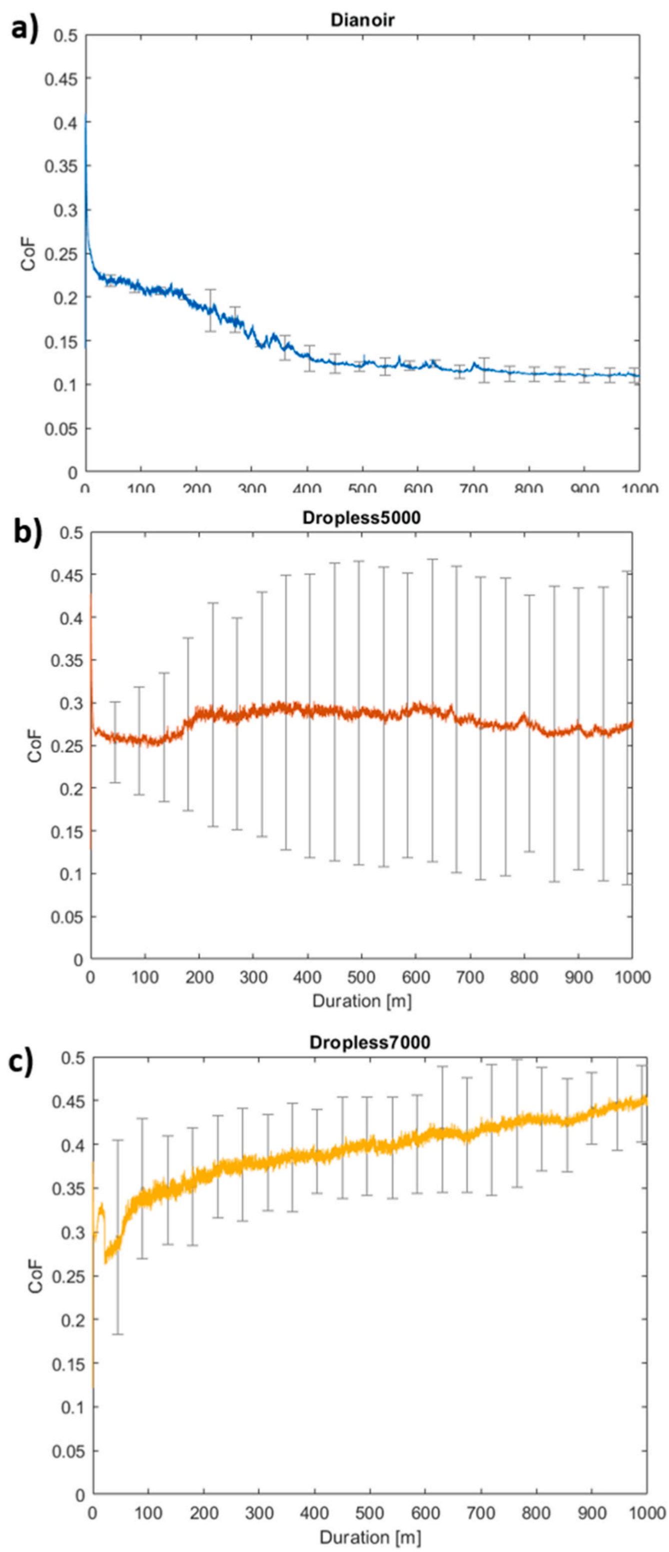

Fig. 11. Average friction curves for the movement against the 6 mm steel ball for the three DLC coatings.

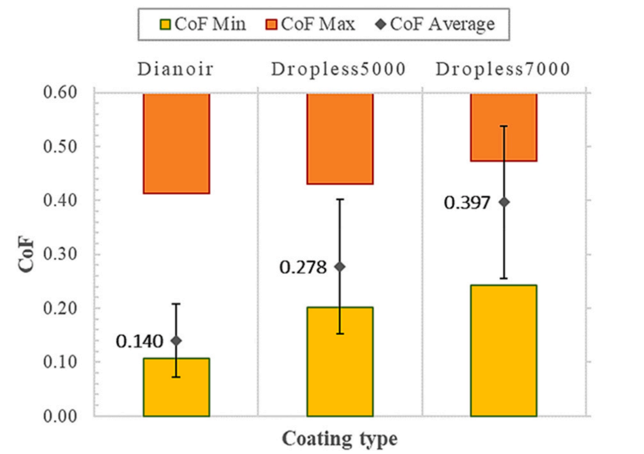

Fig. 12. Average, maximum, and minimum friction values recorded during the test. The average values were calculated excluding the first 50 m of the tests.

characterise the wear behaviour of the coatings; both the friction curve and the amount of material removed due to wear were analysed. The wear calculation was carried out according to the ISO 18535:2018 standard guidelines.

Friction tests A and *B* were performed to investigate the tribological response of the coatings under variable loads and speeds. Only the CoF signal was recorded during the friction tests, while the amount of wear was not measured. A pre-sliding phase was applied for both cases A and B to prepare the contact surfaces and reduce the effect of the accumulation of wear on the friction results. The pre-sliding period lasted 110 m, and it was run with the same parameters as those used for the wear tests. The tangential speed load was then changed, and each loading or speed step lasted 3 min.

Each test was repeated twice on the same sample, once on the front side and once back side, to maintain the same radius as the wear track after several repetitions. At the end of each test, an optical microscope inspection, SEM inspection, EDS analysis, and profile acquisition of the worn-out regions were performed on both the samples and the sphere. The profilometric data allowed the amount of wear to be measured, according to approximated equations of the ISO 18535:2018 standard. Any wear debris was blown away from the contact surfaces before the SEM and EDS analysis, without any further cleaning of the surfaces with acetone.

3. Results and discussion

3.1. Optical microscope, SEM and EDX analyses

The inspection performed on bare steel at increasing magnification across the entire surface of the sample revealed a uniform microstructure constituted by fine carbides uniformly dispersed in a martensitic matrix. A representative image of the microstructure is reported in Fig. 2.

All the exposed surfaces of the discs were coated, as shown in Fig. 1.

A field-emission-gun scanning electron microscope was used to observe the surface morphologies, especially the defects on the DLC layers. None of the samples were sputter-coated for the morphological analysis to avoid any artefacts due to conductive coating deposition. Low and high-magnification SEM images were acquired for the Dropless

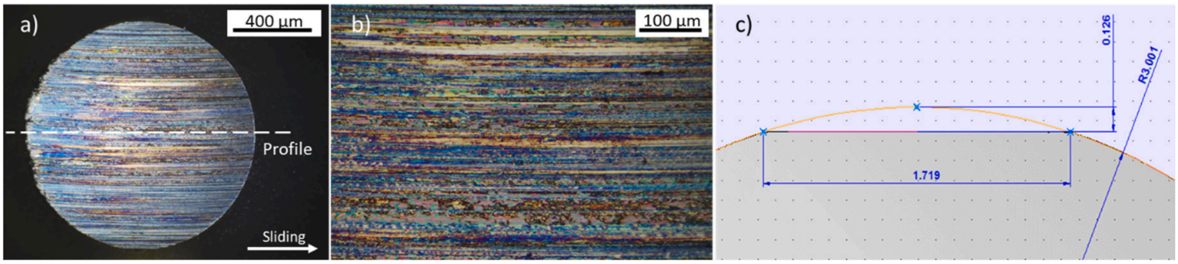

Fig. 13. (a) Worn-out region of the steel ball abraded against Dropless 5000 after 1000 m sliding; (b) Central part of the worn-out region of the sphere inspected under the optical microscope; (c) Profilometric analysis of the steel ball.

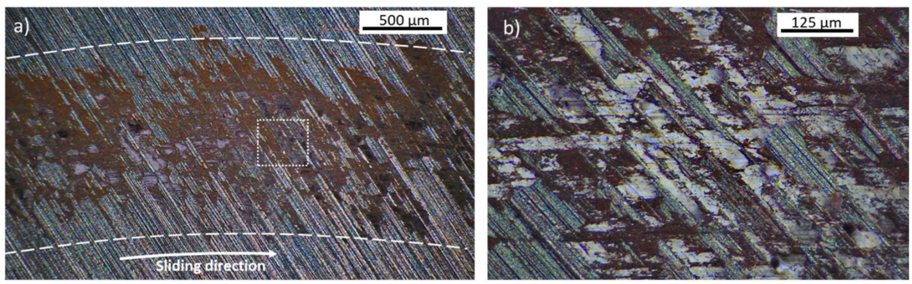

Fig. 14. (a) Sliding region on the sample coated with Dropless7000 after 1000 m sliding; (b) enlarged view of an adhered third body transferred during the wear test as observed under the optical microscope.

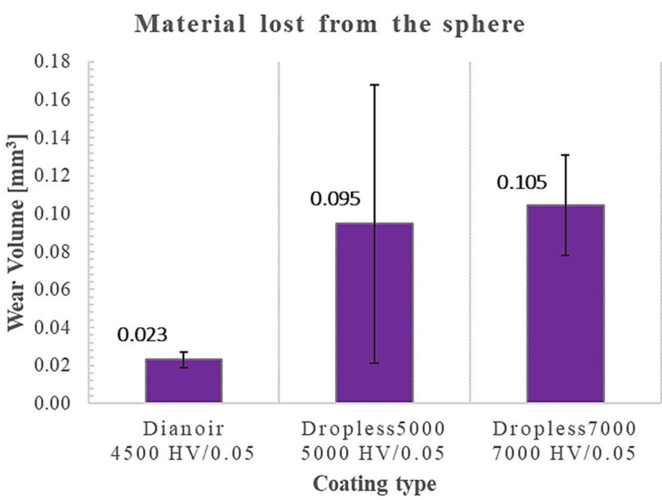

Fig. 15. Amount of wear at the end of the wear test performed according to ISO18535:2018.

5000, Dropless 7000, and Dianoir coatings, and they are reported in Fig. 3. The figures show top-view images of the DLC coatings on steel substrates. The SEM observations evidenced the presence of a smooth, uniform coating, which perfectly followed the morphology of the pristine steel substrate.

Clusters of minor or isolated circular morphological defects were observed on all three coatings, even though they were statistically more evident on Dropless 5000 and 7000. Fig. 3c for Dropless 5000 shows a circular morphological defect with an average diameter of about 20 µm. Similar defects can be detected on Dropless 7000 and Dianoir; the defects in these coatings show a more irregular shape than those detected on Dropless 5000.

Moreover, the coverage of the substrate appears complete and continuous, thus a homogeneous coating has been obtained, even at the sample edges, at least from top view of sample surface. The SEM magnification of a cross-section is shown in Fig. 4; itshows homogeneous and compact coating, but in some cases the films are not so regular and even thus justifying friction results, as discussed below.

One of the main challenges of obtaining a suitable coating is related to the compatibility and adhesion of the substrate to DLC coatings. It appears, from the morphological observations, that the interface between the coating and the substrate is continuous, without any porosity or cracks that could be detrimental for tribological applications.

A higher magnification of the interface area is shown in Fig. 5, where it is possible to observe that the adhesion of the coating to the metallic substrate is good, and it is not possible to distinguish a specific structure (e.g., columnar or others). In fact, no defects resulting from the sectioning and preparation of the sample were observed at the interface. This evidence further demonstrates the robustness of the coating adhesion.

Fig. 4 refers to Dianoir (1 µm); the figure can be assumed, in terms of morphology, to be representative of the other two coatings, i.e Dropless 5000 and Dropless 7000. The thickness of the coating appears to exceed 1 µm, probably due to the presence of an artefact of the cross-section observation and not to complete coplanarity of the substrate and the coating.

The elemental compositions of the DLC coatings deposited on the steel substrate were measured by means of EDS (Fig. 4), which confirmed the presence of C and a negligible amount of Fe, in agreement with the XRD measurements (see below).

In conclusion, no statistically relevant defects or impurities on the DLC layers were observed when using electronic microscopy and EDS mapping.

X-ray diffraction was used to determine the phase composition of the

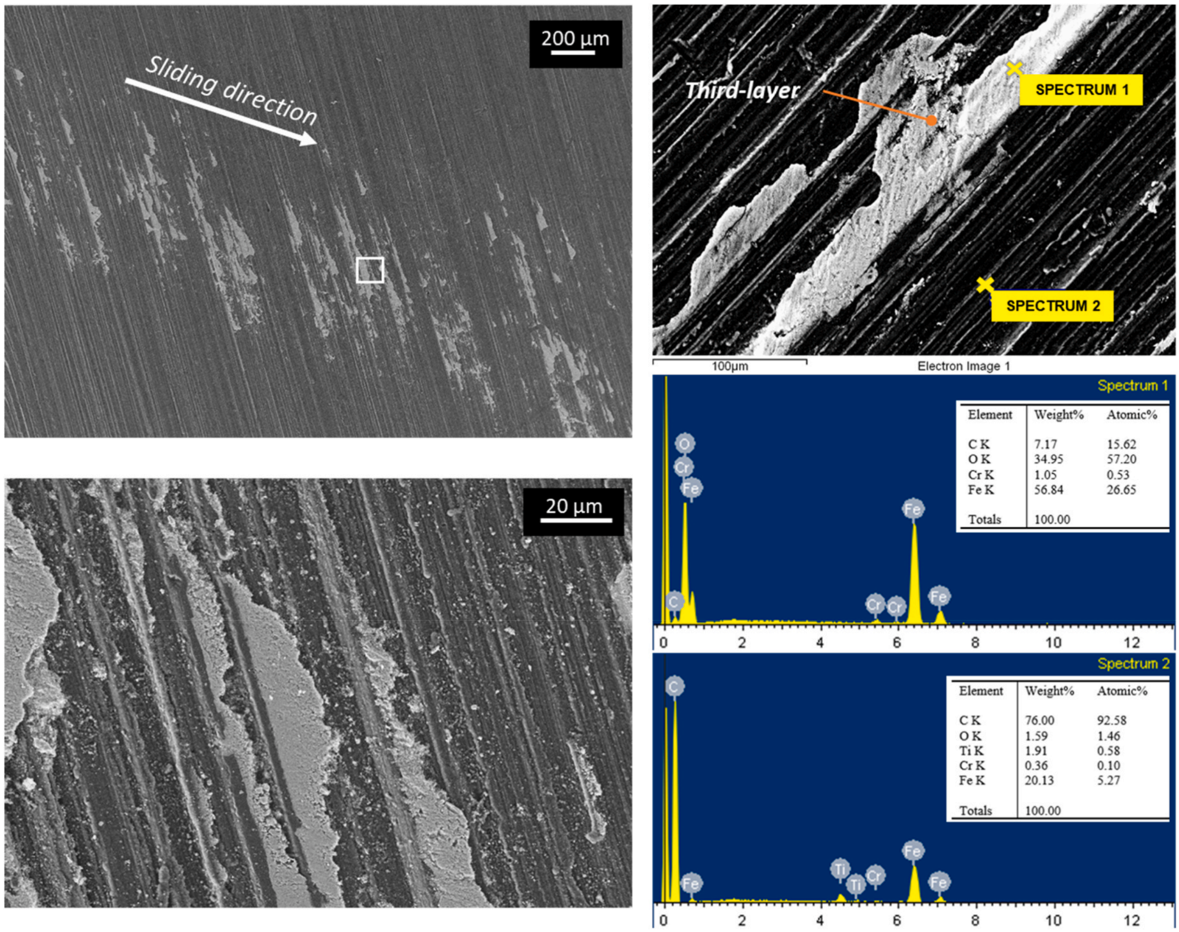

Fig. 16. SEM - EDS analysis of the sample coated with Dianoir after the wear tests.

DLC coatings. The X-ray diffraction performed on the DLC films using conventional θ/2θ scanning methods generally produced a weak signal from the film and an intense signal from the substrate, due to the limited thickness of the analysed coatings.

It should be mentioned that the X rays penetrated the DLC layer, and the crystalline phases of the substrate were detected; the diffraction spectra obtained in this way (not reported here) exhibited martensite and austenite peaks. The detected austenite is retained austenite. A grazing incidence scan was performed on coated samples to avoid the presence of an intense signal from the substrate and to obtain a stronger signal from the film, with a lower incidence angle for the total reflection of the film, without any substrate interference (Fig. 6). The XRD pattern obtained from the analysis of bare steel is also reported. A discernible peak was noted at 2ϴ~ 44° for the coated samples, which may correspond to an sp^3 diamond plane, and this peak could easily overlap the peak of the steel substrate. However, no peaks of retained austenite and low peaks of martensite were observed for the DLC-coated samples.

According to the supplier's specifications and in accordance with microscopic analysis reported in Fig. 2, the predominant phase in the bare steel is martensite.

3.2. Scratch tests

Fig. 7 provides an overview of the critical loads, LC1 and LC2, of Dropless 5000, Dropless 7000, and Dianoir obtained from the scratch tests. Fig. 8 shows the critical loads and scratch crack propagation resistance of the coatings. The same failure deformations were observed for all the coatings under the optical microscope. Deformation of the coating started with cohesive failure, which became visible for all the coatings after reaching a load of between 3 and 4 N. Localised transverse semi-circular cracks, which are typical of brittle fractures, then caused the coating to collapse, due to compressive pressures ahead of the advancing indenter, while plastically piled-up material from substrate deformation increased the failure rate. The second highest critical load was measured for Dropless 5000. As far as toughness is concerned, the lowest CPR value, that is, of 88.76, was obtained for Dianoir, while no significant differences were observed between Dropless 5000 and Dropless 7000, which showed 123.67 and 130.09, respectively. Dropless 5000 and Dropless 7000 are both characterised by more toughness than Dianoir.

Fig. 9 shows the obtained 3D profilometry images, while Fig. 10 indicates the 2D surface profiles of the scratched samples. 3D maps were taken in the area around 30 N, while the 2D profile was extracted at 30 N, which corresponds to the normal load close to Lc2. It can be observed, from a comparison of the morphology of the scratch paths, that the substrate coated with Dianoir displays more significant plastic deformation than Dropless 5000 and 7000. Dianoir suffered higher shear stress during the scratch test, which caused the material to pile up. This could be related to the lower coating hardness of Dianoir.

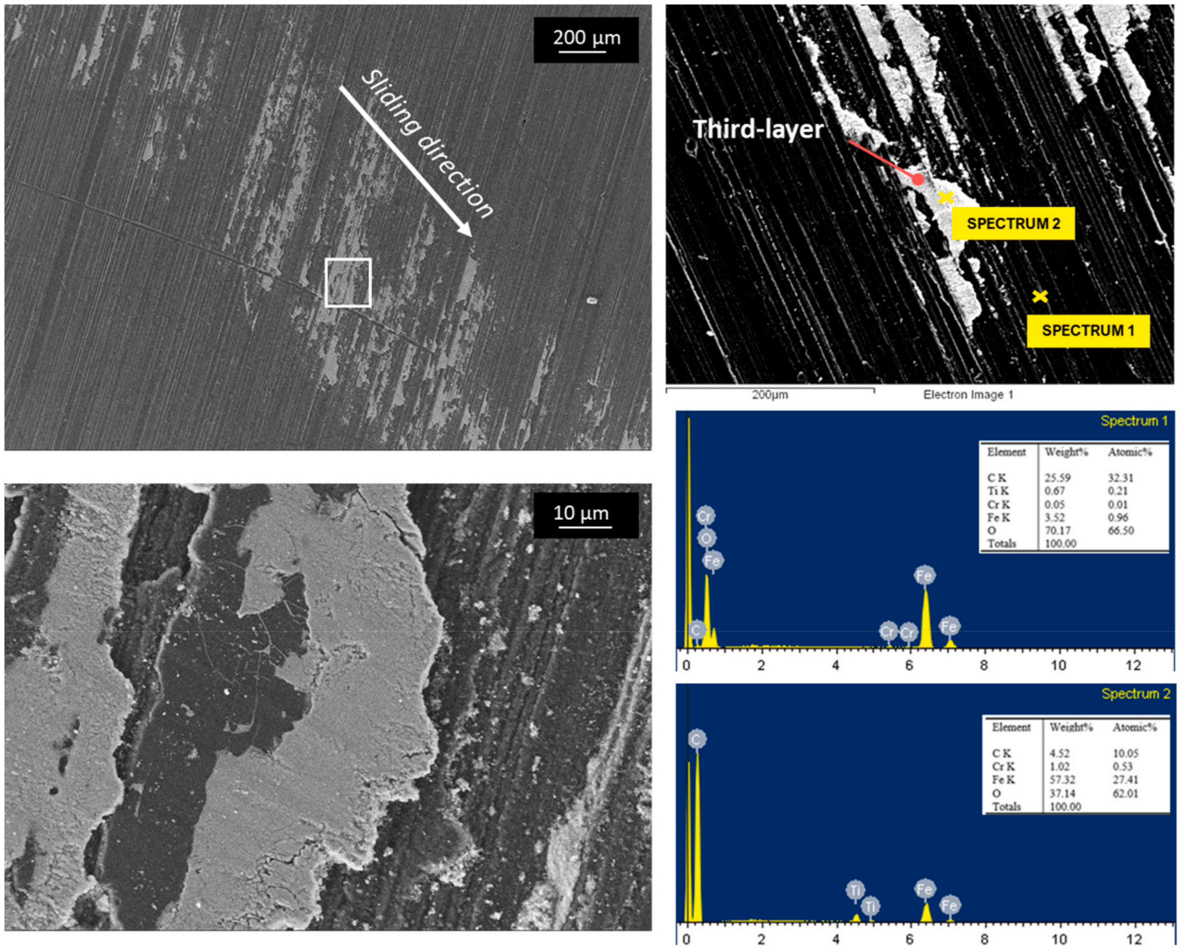

Fig. 17. SEM - EDS analysis of the sample coated with Dropless 5000 after the wear tests.

3.3. *Tribological tests*

3.3.1. *The ISO18535:2018 wear test*

Fig. 11 a,b and c show the average friction curves recorded during the wear tests for the movement against the AISI 52100 steel ball. The rough friction curves were filtered with a 15-point moving average filter to reduce noise. The figures report the error bars to highlight the actual scattering of the results compared to the averaged friction curve.

The outcome of the wear tests revealed a very different tribological behaviour of the three coatings against steel. Dianoir featured a slowly decreasing friction coefficient that stabilised at about 0.11–0.12 in the second half of the test. Dropless 5000 produced a relatively stable friction curve at about 0.27 over the duration of the test. Dropless 7000, the hardest of the three DLC coatings investigated in this paper, showed the opposite behaviour. The coefficient of friction increased from 0.3 to about 0.45, due to the wear of the counterpart.

Fig. 12 summarises the representative CoF values (overall average, minimum, and maximum) for the three coatings according to the ASTM G99-17 standard guidelines for pin-on-disc tests. The average values were calculated excluding the initial wear-in phase, i.e., the first 50 m of sliding.

The profiles of the worn-out region and the images taken under the optical microscope showed that the sphere suffered from a high level of wear due to abrasion (Fig. 13). The hard carbon coatings instead basically suffered no damage, as no wear track was visible from the profilometric inspection, and just some traces of adhered matter from the sphere were observed under the microscope, as shown in Fig. 14.

The amount of material removed by the steel ball during the wear test, plotted in Fig. 15, is correlated with the hardness of the coating (see Table 1). The harder the carbon layer is, the stronger the abrasive effect on the steel counterpart, i.e., the higher the quantity of debris produced and transferred onto the carbon coating during the sliding interaction. The highest scattering of wear appeared for Dropless 5000 against steel; this erratic behaviour over the repetitions of the wear test may be related to an inhomogeneous hardness of the DLC layer due to an inhomogeneous DLC deposition on the upper and lower faces of the sample.

Figs. 16–18 present the results of the SEM-EDS analyses on the coated samples inside and outside the sliding path. The same analyses were also performed on the spheres, and the results are reported in Appendix A. The analysis of the worn-out surfaces revealed that a third body, made up of oxides, formed along the sliding path, and filled the surface roughness ridges. The build-up of this third layer was more extensive for Dropless7000 and less so for Dianoir. This confirms the inherent frictional behaviour reported in Fig. 11. The initial steel-DLC contact interface for Dropless 7000 and Dropless 5000 evolved to a steel-oxide-DLC interface with a poor tribological performance (for

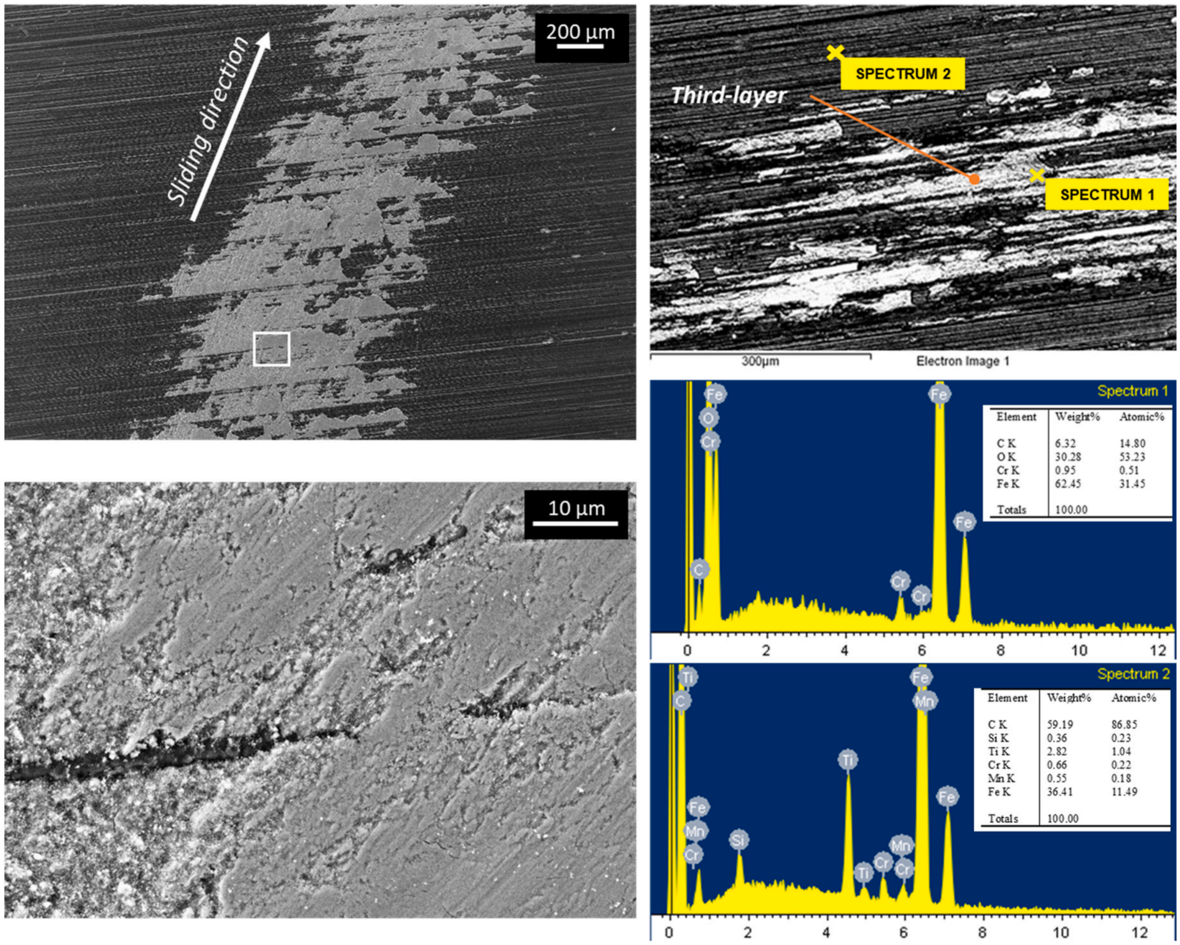

Fig. 18. SEM-EDS analysis of the sample coated with Dropless 7000 after the wear tests.

example, the typical CoF value of steel-steel contact is known to be about 0.6 due to the formation of an oxide layer in between the two surfaces). The SEM magnification reported in Fig. 17 proves that large O, Fe, and Cr contents were detected along the sliding path, both on islands of adhered material and elsewhere along the sliding path. Moreover, the coefficient of friction increased, in part because of the substantial widening of the contact area due to wear.

In the Dianoir case, the steel-carbon interface was preserved throughout the test, since only a limited part of the sliding path was covered by oxides (Fig. 16), and the C content outside the islands of the adhered material, detected by means of EDS, was dominant over O, Fe, and Cr. The carbon content increased inside the worn region of the sphere (see Appendix A), thus suggesting that a little carbon may have been transferred onto the steel disc.

3.3.2. Friction test

Fig. 19 reports the results of *Friction Test A* performed under a variable load. The initial 110 m of the pre-sliding distance was not considered in the analysis as it served as a running-in phase for the contact interface.

The results show that the tribological behaviour of the compared DLC coatings varies and is correlated with their degree of hardness. Dianoir and Dropless5000 showed similar friction coefficient values, which increased as the load increased. The CoF grew by a factor of almost 1.5 between 3 N and 15 N, as shown in Fig. 19. More scattering occurred under a very low load because the low contact pressure probably led to unsteady contact dynamics in the presence of wear debris. Consequently, the Dropless5000 trend reversed over the 1 N–3 N load range, compared to Dianoir. Nevertheless, the CoF measured for Dropless7000 was always the highest, although its value was halved between 1 N and 15 N.

An overview of the results of *Friction Test B,* performed under variable speeds, is presented in Fig. 20. It can be observed that the speed in general had little impact on friction. Minor fluctuations of the CoF value were observed for Dianoir and Dropless 5000 over the speed range investigated in this study. Like the Friction Test A, the CoF of the friction measured for Dropless7000 was always higher than that of the other two coatings, and its value dropped by 20% for a 50-fold increase in speed. This behaviour might be due to the increase in temperature at the sliding interface, which would seem to suggest a temperature-sensitive characteristic of Dropless7000.

4. Conclusions

This work has compared three types of commercial DLC coatings (Dianoir, Dropless 5000 and Dropless 7000), deposited onto AISI 52100

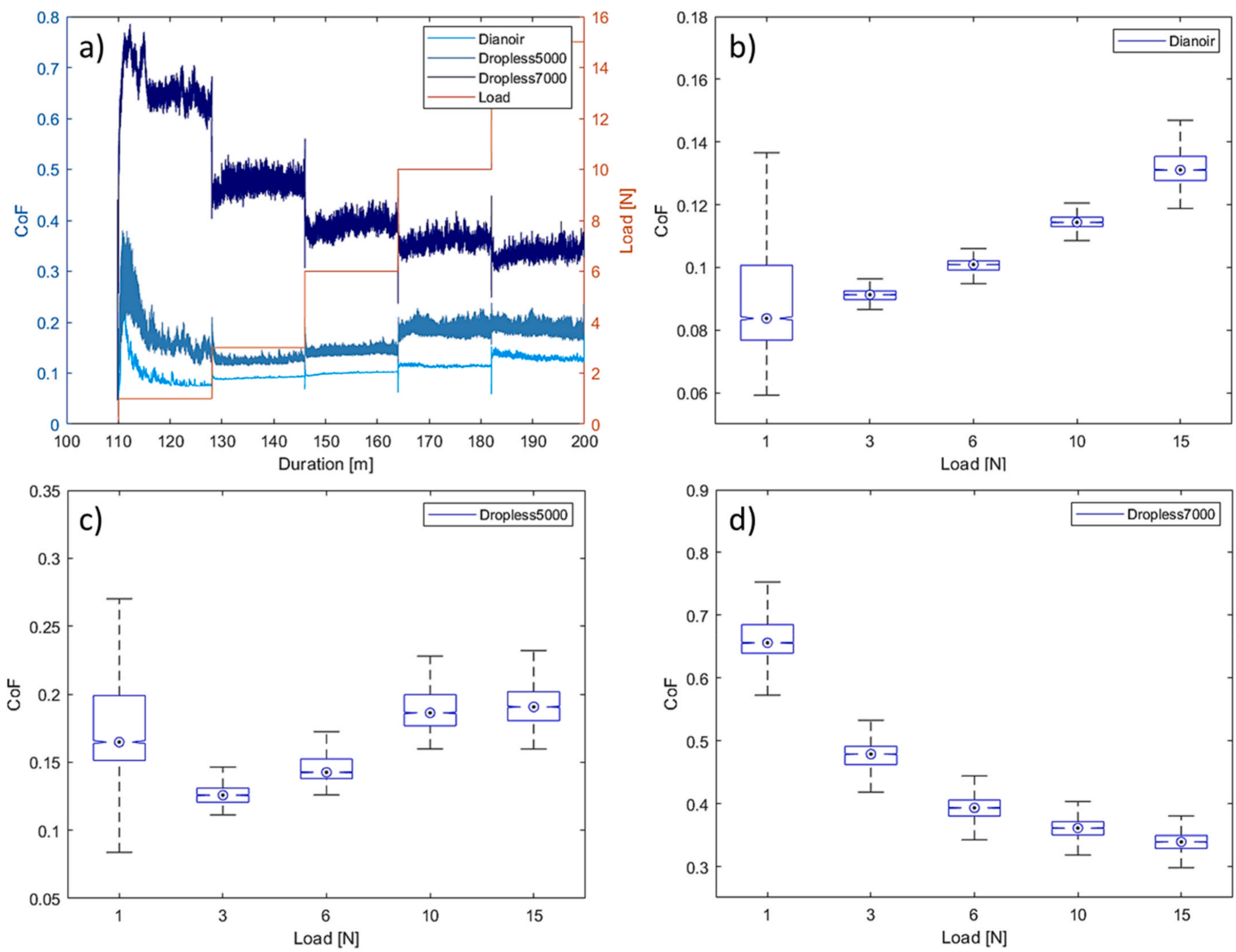

Fig. 19. (a) Rough friction curve recorded for Friction test An under increasing load and a constant speed of 0.1 m/s (b–d) Summary statistic box plots for Dianoir, Dropless5000, and Dropless7000, respectively. The blue dot inside each box represents the median value of the load level. Each loading step lasted 3 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

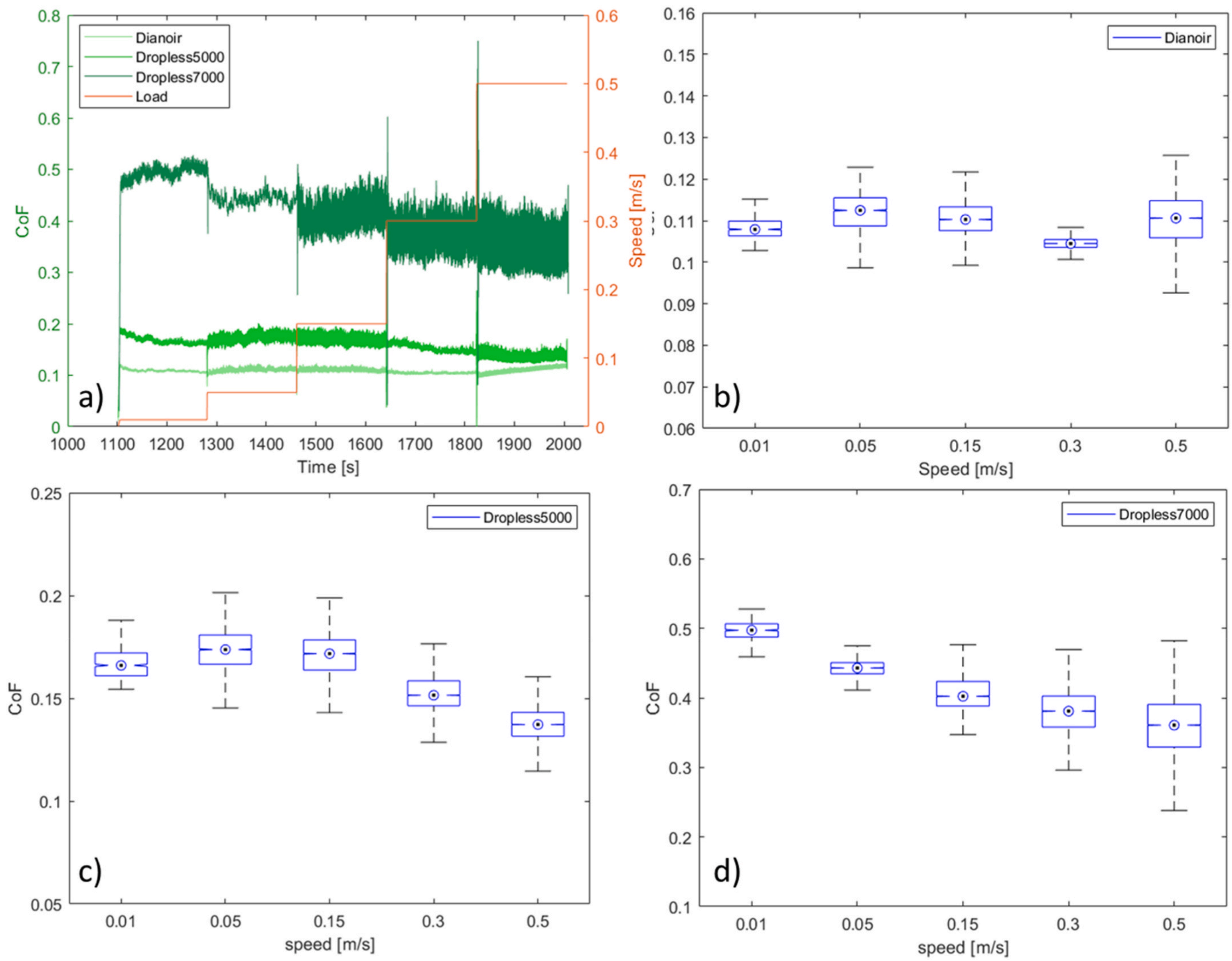

Fig. 20. (a) Rough friction curve recorded for Friction test B under an increasing speed and constant 5 N load; (b–d) Summary statistic box plot for Dianoir, Dropless5000, and Dropless7000, respectively. The blue dot inside each box represents the median value of the speeds. Each speed step lasted 3 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

steel discs, to investigate their tribological performances in terms of friction reduction, wear resistance, and adhesion. The tribological properties were investigated by means of the scratch and pin-on-disc tests. The disc surfaces were analysed by means of 3D profilometry, SEM, and X-ray diffraction.

The results of the scratch tests showed the lowest toughness value for Dianor, while Dropless 5000 and Dropless 7000 had similar values. However, pin-on-disc tests revealed a different tribological behaviour for the three coatings: Dianoir featured a slowly decreasing friction coefficient that then stabilised, Dropless 5000 showed a stable friction curve throughout the tests, whereas Dropless 7000 produced a coefficient of friction that gradually increased from the start to the end of the test. Overall, Dianoir showed the lowest coefficient of friction.

As far as wear is concerned, the three coatings were not damaged by the sphere, while the steel balls instead resulted in a large amount of worn material. The ball moved against the Dianoir coating produced the smallest amount of removed material, the one moved against Dropless 7000 resulted in the highest amount, and the wear volume was closely correlated with the hardness of the coatings.

The results have generally shown excellent performances for the three DLC coatings regarding their mechanical and tribological properties. It is possible to conclude that these three coatings may be successfully applied to many mechanical components to reduce friction and wear. Dianoir seems the best choice whenever sliding motion prevails, due to the low CoF witnessed for a wide range of loads and speeds. On the other hand, Dropless 5000 and Dropless 7000 appear to be more suitable for rolling motion, for instance, for bearings where surface fatigue dominates, thanks to their elevated toughness, and their higher adhesion and wear resistance.

The study explored the tribological properties of three DLC coatings, typically used for decorative applications, through scratch and pin-on-disc tests. Results suggest that these coatings have potential for broader mechanical applications, including reducing friction and wear in components like bearings, cutting tools, and power transmission mechanisms, taking advantage of some practical issues, such as surface quality finishing and the expertise in depositing them on complex geometries.

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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Appendix A. EDS analysis of the steel spheres used for the tribological test

Figures A1 to A3 report the SEM images and the results of the EDS analysis performed on the steel spheres after the tribological test inside and outside the flattened worn-out region. Interestingly, a higher content of elemental carbon was never detected inside the worn-out region of the sphere. Therefore, the transfer of graphite-like carbon can be excluded under the present testing conditions.

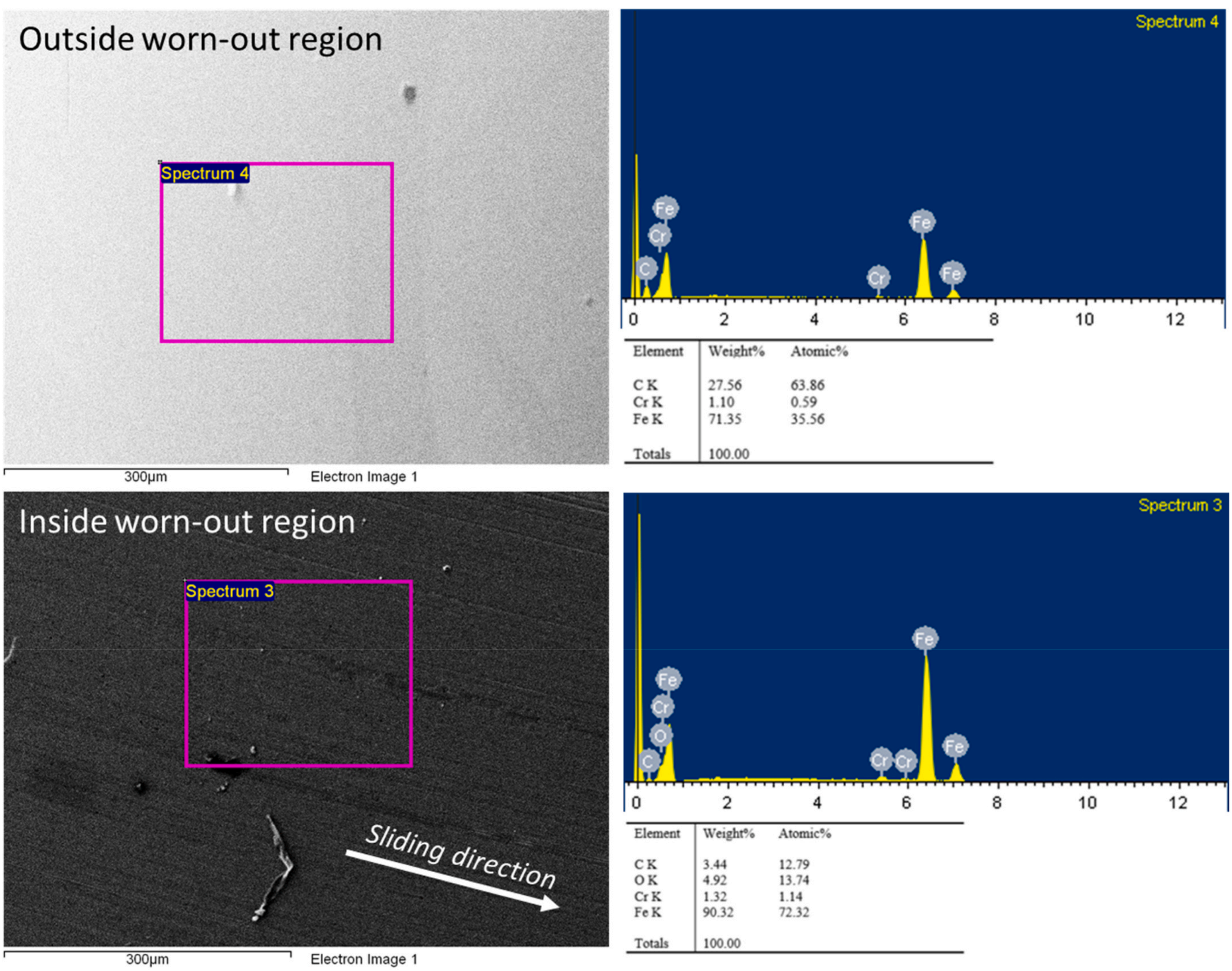


Fig. A1. SEM - EDS analysis of the steel sphere against Dianoir DLC after the wear test.

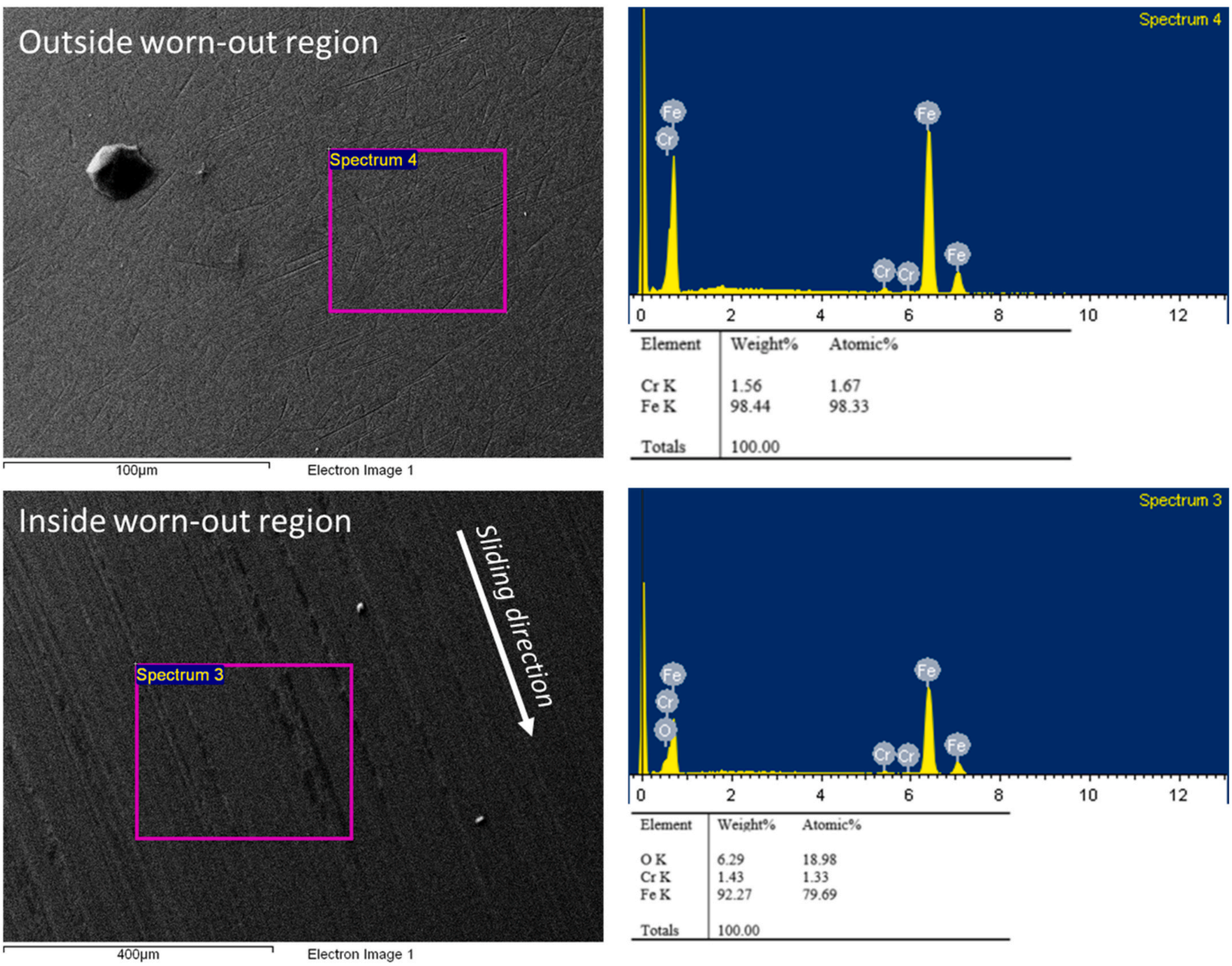
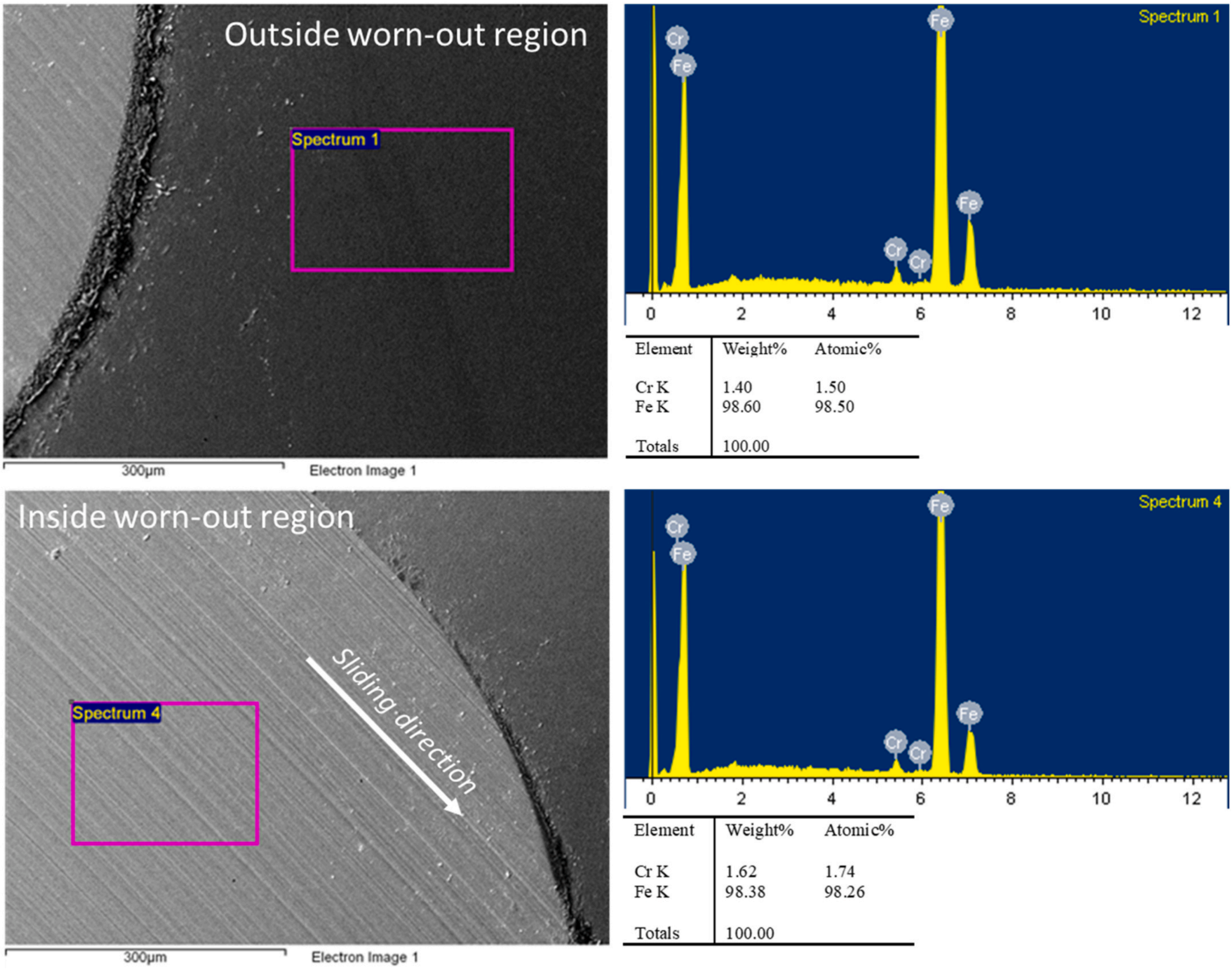


Fig. A2. SEM - EDS analysis of the steel sphere against Dropless5000 DLC after the wear test.



Element	Weight%	Atomic%
Cr K	1.40	1.50
Fe K	98.60	98.50
Totals	100.00	

Element	Weight%	Atomic%
Cr K	1.62	1.74
Fe K	98.38	98.26
Totals	100.00	

Fig. A3. SEM - EDS analysis of the steel sphere against Dropless7000 DLC after the wear test.

References

[1] Y. Xiao, W. Shi, J. Luo, Y. Liao, The tribological performance of TiN, WC/C and DLC coatings measured by the four-ball test, Ceram. Int. 40 (2014) 6919–6925.

[2] F. He, P. Wong, X. Zhou, Wear properties of DLC-coated steel rollers running with highly contaminated lubrication, Tribol. Int. 43 (5–6) (2010) 990–996.

[3] E. Marin, A. Lanzutti, M. Nakamura, M. Zanocco, et al., Corrosion and scratch resistance of DLC coatings applied on chromium molybdenum steel, Surf. Coat. Technol. 378 (2019), 124944.

[4] E. Dalibón, J. Nahuel Pecina, M. Moscatelli, M. Ramírez Ramos, et al., Mechanical and corrosion behaviour of DLC and TiN coatings deposited on martensitic stainless steel, J Bio- and Tribo-Corr 5 (2019) 34.

[5] J. Vetter, 60 years of DLC coatings: historical highlights and technical review of cathodic arc processes to synthesise various DLC types, and their evolution for industrial applications, Surf. Coat. Technol. 257 (2014) 213–240.

[6] A. Zia, M. Birkett, Deposition of diamond-like carbon coatings: conventional to non-conventional approaches for emerging markets, Ceram. Int. 47 (2021) 28075–28085.

[7] C. Treutler, Industrial use of plasma-deposited coatings for components of automotive fuel injection systems, Surf. Coat. Technol. 200 (2005) 1969–1975.

[8] A. Ferrari, Diamond-like carbon for magnetic storage disks, Surf. Coat. Technol. 180–181 (2004) 190–206.

[9] K. Bewilogua, D. Hofmann, History of diamond-like carbon films — from first experiments to worldwide applications, Surf. Coat. Technol. 242 (2014) 214–225.

[10] R. Gåhlin, M. Larsson, P. Hedenqvist, ME-C:H coatings in motor vehicles, Wear 249 (2011) 302–309.

[11] D. Rajak, A. Kumar, A. Behera, P. Menezes, Diamond-like carbon (DLC) coatings: classification, properties, and applications, Appl. Sci. 11 (2021) 445.

[12] P. Dearnley, A. Elwafi, R. Chittenden, D. Barton, Wear and friction of diamondlike-carbon coated and uncoated steel roller bearings under high contact pressure oil lubricated rolling/sliding conditions, J. Tribol. 136 (2) (2014), 021101.

[13] W. Tillmann, N. Lopes Dias, D. Stangier, L. Hagen, et al., Tribo-mechanical properties and adhesion behavior of DLC coatings sputtered onto 36NiCrMo16 produced by selective laser melting, Surf. Coat. Technol. 394 (2020), 125748.

[14] B. Coll, M. Chhowalla, Amorphous diamond film by enhanced arc deposition, Surf. Coat. Technol. 79 (1–3) (1996) 76–86.

[15] H. Han, F. Ryan, McClure, Ultra-thin tetrahedral amorphous carbon film as slider overcoat for high areal density magnetic recording, Surf. Coat. Technol. 120–121 (1999) 579–584.

[16] P. Yan, S. Yang, B. Li, et al., Deposition of diamond-like carbon films on an iron substrate by a pulsed high-density plasma beam at room temperature, Mater. Chem. Phys. 45 (2) (1996) 167–170.

[17] S. Wagal, E. Juengerman, C. Collins, Diamond-like carbon films prepared with a laser ion source, Appl. Phys. Lett. 53 (1988) 187–188.

[18] T. Sato, S. Furuno, S. Iguchi, M. Hanabusa, Deposition of diamond-like carbon films by pulsed-laser evaporation, Jpn. J. Appl. Phys. 26 (1987), L1487.

[19] Y. Liou, R. Weimer, D. Knight, R. Messier, Effect of oxygen in diamond deposition at low substrate temperatures, Appl. Phys. Lett. 56 (1990) 437–439.

[20] C. Meunier, F. Munnik, J. Stauffer, E. Germann, S. Mikhailov, Dual FCVA–PECVD deposition for DLC films, Thin Solid Films 482 (2005) 197–200.

[21] J. Robertson, Diamond-like amorphous carbon, Mater. Sci. Eng. R Rep. 37 (2002) 129–281.

[22] C. Donnet, Recent progress on the tribology of doped diamond-like and carbon alloy coatings: a review, Surf. Coat. Technol. 100–101 (1998) 180–186.

[23] D.K. Rajak, A. Kumar, A. Behera, P.L. Menezes, Diamond-like carbon (DLC) coatings: classification, properties, and applications, Appl. Sci. 11 (2021) 4445.
[24] H. Moriguchi, H. Ohara, M. Tsujioka, History and applications of diamond-like carbon manufacturing processes, SEI Tech. Rev. 82 (2016).
[25] A. Vanhulsel, F. Velasco, R. Jacobs, L. Eersels, D. Havermans, et al., DLC solid lubricant coatings on ball bearings for space applications, Tribol. Int. 40 (2007) 1186–1194.
[26] L. Xia, G. Li, The frictional behavior of DLC films against bearing steel balls and Si3N4 balls in different humid air and vacuum environments, Wear 264 (2008) 1077–1084.
[27] S. Wu, H. Kousaka, S. Kar, D. Li, J. Su, Friction and wear performance of bearing ball sliding against diamond-like carbon coatings, Mater. Res. Express 4 (2017), 015602.
[28] V.N. Inkin, S.I. Ukhanov, K.A. Yakovlevich, Patent, A METHOD for FORMING A SUPERHARD AMORPHOUS CARBON COATING IN VACUUM, 2004. WO/2004/104263EPO, Applicants ARGOR ALJBA SA [CH].
[29] S. Patent Ukhanov, Method to filter macro particles in a cathodic arc physical vapor deposition (PVD), in: VACUUM, 2005. WO2015173607 Applicants ARGOR ALJBA SA (CH).
[30] S.A. Argor-Aljba [Online]. Available: www.argor-aljba.com.
[31] R. Akhter, Z. Zhou, Z. Xie, P. Munroe, TiN versus TiSiN coatings in indentation, scratch and wear setting, Appl. Surf. Sci. 563 (2021), 150356.