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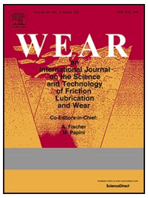

Influence of the alloying elements on the tribological performance of DLC coatings in different sliding conditions

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ABSTRACT

Reduction of friction and wear at the sliding surfaces are the main concern in several applications. From an extensive list of low friction hard coatings, DLC type is one of the most studied and develop for achieving low wear and friction. The addition of an alloying element is extensively used, since it can change significantly the coatings performance. Therefore, in this research the tribological behaviour of DLC coatings alloyed with different elements was evaluated, since no works comparing the tribological properties of DLC films with approximately the same alloying elements concentration are reported in the literature. The coatings were deposited by physical vapor deposition and alloyed with: tungsten (W), silver (Ag), silicon (Si), silicon and oxygen (SiO), with concentrations of metallic elements between 10 and 15 at. % and a pure DLC coating was also deposited for comparison purposes. The coatings hardness varied between 23 GPa for the pure DLC and 11 GPa for the alloyed with Si and O. The tribological behaviour of the coatings was evaluated by pin-on-disk against 10 mm 100Cr6 steel balls, at room temperature (RT) and 100 °C. The best wear resistance was achieved with the pure DLC and DLC-W for RT tests. At RT the lowest friction was obtained with the DLCSi and DLCSiO coatings. Despite of the low COF values, those coatings displayed the highest specific wear rate values among all the films. This is attributed to the presence of hard SiC particles stick at the ball counterpart which promotes severe abrasion of the coatings surface. The increase of the temperature to 100 °C increases significantly the friction coefficient for the DLC and DLC-W coatings, whilst, for DLC-Ag, DLC-Si and DLC-SiO coatings a slight decrease is noticed. At this temperature DLCAg coating is the more performing due to the formation of a tick tribolayer rich in Ag adhered at the counterpart surface. With this work it was concluded that friction and wear are not directly related, and the third bodies formed on the sliding surfaces have major influence on the tribological performance of the system.

1. Introduction

The reduction of friction and wear at the sliding surfaces are the main concern in several applications. Nowadays, thin films deposition is a well establish method to achieve this goal. From an extensive list of low friction hard coatings, DLC type is one of the most studied and developed for achieving low wear and friction. As a consequence of this intensive research, a myriad of DLC coatings with a wide range of properties are available on the market. Therefore, the selection of the coatings that are best suited for a specific application is not an easy process, since DLC coatings can present a wide range of properties [1]. DLC coatings can be deposited by different processes such as CVD, PVD or arc discharge, among others, resulting in a wide spam of properties [2]. Alloying DLC coatings with other elements is another method used to modify de properties of C base coatings, the most used are hydrogen and metals. This makes the selection of the coating best suited for a specific application very difficult to do, thus, it may require some trial tests from a set of coatings, to select the best one. This may result in increasing costs for the implementation of the best solution.

The deposition of metal doped DLC coatings by PVD methods, has been proven to be an effective process to modify the coatings properties, particularly the ones that influences the tribological behaviour. Concerning the doping elements, DLC coatings can be divided in two main groups: i) non-carbide formers such as Cu or Ag [3–6], and ii) carbide

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formers, such as, Cr [7–9] Ti [10,11], Si [12–14], W [15–17]. Also, there are two doping elements that can have significant influence on the tribological performance of DLC coatings, i.e. H and O. The hydrogen is extensively used, since in most of the times is always present in the gases used to produce DLC coatings by CVD. Also by PVD reactive magnetron sputtering metal doped DLC coatings are deposited from a metal target in a reactive atmosphere of Ar with a gas containing C and H (normally methane or acetylene) resulting in deposition process more efficient and with less costs, since with just one cathode it is possible to make the deposition of DLC doped coatings [2]. The O is much less used in the deposition of DLC type coatings, however, it is frequently present in the tribological processes of the coatings and it can have a significant role on the formation of a transfer layer or third body in the sliding process [12].

The tribological behaviour of DLC type coatings presents an impressive spam of friction coefficients in dry sliding. It can reach high values of coefficient of friction >0.4 [18], to very low values of 0.008 [19]. This wide range of values is related with the coatings characteristics, the properties of the sliding counterparts, the tribotest settings and the environmental conditions. As result, the same coating can present different levels of friction just by changing the test conditions. Also, the DLC type coatings presents an wide range of wear rates that can be low as 0.00046×10^{-6} mm^3/Nm in Ar environment testing [20].

The PVD deposition process is one of the most used concerning the industrial implementation of DLC coatings, particularly in DLC metal doped coatings due to its easy implementation, i.e. it is only necessary to add one more metal target or some metal pellets pellets one of the targets of C to produce the doped coatings.The selection of the doping element must take in consideration the application in which is intended to use the coated part, since the elements added to the DLC type coating can modify significantly the tribological behaviour of the coating. For instance, the Ag-DLC type coatings are developed due to its bactericide behaviour for potential use in biological applications [21], maintaining the excellent tribological behaviour common to the DLC type coatings.

Another alloying element used to modify the properties of this type of coatings is the W. This element can improve the tribological performance of the system in lubricated contact with formulated oils [22,23]. Also, addition of tungsten have shown to improve the tribological behaviour of the coatings at higher temperatures [24] maintaining the low values of friction and wear.

Other element that is also often used as an alloying element in the DLC type coatings is the Si. Alloying the DLC coatings with Si enhances their thermal stability due to the stabilization of the disorder carbon structure, with the formation of thermally stable Si–C sp^3 bonds [25]. Another important feature of Si alloyed coatings is the reduction of friction and its excellent tribological behaviour at high temperatures [12,26]. The low friction behaviour observed at high temperatures is related with the formation of a transfer layer mainly composed of Si oxides [12]. This was also confirmed with the study the influence of the addition of O in the coatings composition with the lowest friction observed for the higher O content in the coatings composition [13].

Although the composition and structure of DLC type coatings have major influence on the tribological performance, the environmental and test conditions also plays an important role on their friction and wear behaviour. The humidity or the environment can influence the friction and wear behaviour of the coatings. For instance in the case of non-hydrogenated DLC coatings tested against aluminium or WC balls, the increase of the moisture in the atmosphere result in a decrease of wear and friction [27]. However just by changing the coatings composition, hydrogenated and non-hydrogenated, different trends were observed with the increase of the moisture, with low wear and friction at low levels of humidity in the case of DLC-H; and high levels of wear and friction with low levels of humidity for non-hydrogenated DLC coatings [28]. The temperature is another important factor concerning the tribological performance of this type of coatings. Normally the increase of the temperature increases the wear rate [29]. The tribological performance of DLC type coatings is the result of several conditions, intrinsic and extrinsic, such as composition, structure, morphology, type of bonds, test temperature, environment, humidity, load, sliding speed, type of test and sliding counterpart [30].Therefore, the selection of the coating with the best performance for a specific application is a difficult task.

The aim of this research work is to compare the tribological performance of DLC alloyed coatings with different elements, deposited with the same deposition equipment with similar deposition conditions. At the best knowledge of the authors there is no in the literature works concerning the comparison of alloyed DLC coatings with approximately the same percentage of the alloyed element. Therefore, DLC coatings were deposited in a four cathode Teer coatings deposition chamber alloyed with Ag, W, Si and Si with O. A pure DLC coatings was also deposited for comparison purposes. The coatings were deposited with approximately the same alloying element concentration and the tribological behaviour was studied at two different temperatures (RT and 100 °C) in a pin-on-disk equipment.

2. Experimental details

2.1. Coatings deposition

The coatings were produced in a four cathode Teer Coatings unbalanced magnetron sputtering deposition chamber. The substrates used for the depositions were polished steel disks for the tribological characterization and mirror polished Si substrates. A set of five different carbon base coatings were deposited. A pure DLC coating (named DLC), a tungsten doped DLC (named DLCW), a silver doped DLC (named DLCAg), a silicon doped DLC (DLCSi) and a silicon oxygen doped DLC (DLCSiO). All the coatings were deposited using a similar procedure. In the deposition chamber, two graphite and one Cr targets were mounted for all the coatings. The last target was used to deposit a Cr interlayer. For the alloyed coatings an additional target was used. To the DLCW coating a carbon target with 14 W pellets with 20 mm of diameter distributed evenly in the preferential erosion zone of the target was used (the deposition conditions were set according with a previous work [17]). In the case of the DLCAg coating a similar target was used, however, in this case the number of Ag pellets was 6 due to the higher sputtering yield of the silver. In the case of DLCSi and DLCSiO a full silicon target was used, the depositions conditions were set according to previous work [13]. All four cathodes have the dimensions of 375x175 mm^2. The deposition conditions to deposit the Cr interlayer were identical for all of the 5 coatings used in this research. The power on both pure carbon targets was the same for all of the depositions, while, the power on the carbon target with W or Ag pellets was adjust to have the pretended metal content. In the case of the DLC doped with Si and oxygen (DLCSiO), a reactive atmosphere of O_2 was added. A summary of the deposition conditions for the different coatings is presented in Table 1.

2.2. Coatings characterization

The thickness, surface and cross section morphology of the coatings were analysed in a Field Emission Scanning Electron Microscope (FESEM Zeiss Merlin, Oberkochen, Germany). The chemical composition was assessed using energy dispersive spectroscopy (EDS) in the same microscope. Also, the wear tracks and the steel balls counterparts used in the tribological experiments, were characterized in the same equipment.

The hardness and the reduced Young's modulus of the coatings was assessed by nanoindentation (NanoTest, Micromaterials, Wrexham, UK) using a Berkovich tip. A 10 mN load was used to reach indentation depths of less than 10% of the thickness of the films, in order to minimize the effect of the substrate. For each sample 16 indentation were performed in order to have and reliable statistical value of the measurements.

Table 1
Deposition conditions for the selected coatings. For DLCW the alloying target was a graphite target with W pellets, for the DLCAg was a graphite target with Ag pellets, for the DLCSi, and DLCSiO a full silicon target was used.

Coating	Power C targets (W)	Power alloying target (W)	Substrate Bias	Ar flow (sccm)	O_2 flow (sccm)	Deposition Time (min)
DLC	2x1750	–	−110V	46		470
DLCW10	2x1750	1000	−110V	46		80
DLCAg 10	2x1750	400	−110V	46		160
DLCSi	2x1750	300	−50	35		180
DLCSi420W6O2	2x1750	420	−50	35	16.5	150

Raman spectroscopy was used to evaluate the variations of the carbon bonding characteristics due to the addition of different alloying elements and deposition conditions. For that a Horiba HR800 spectrometer equipped with A He–Cd laser (441.6 nm, Kimmon IK series, Japan) was used. The Acquisition time was 15 s and 5 acquisitions were accumulated (total time 75 s), with a ND1 and a 100x magnification lens. The desconvolution of the Raman spectra was performed with two symmetric Gaussian functions with a linear background in the range 900–1800 cm^{-1}.

The surface topography of the deposited coatings on steel substrates was evaluated by Atomic Force Microscopy (AFM) (Bruker Innova) with a Si tip of nominal 6 nm radius used in contact mode. Several scans were acquired on the surface of each coating to ensure surface representation. The Height-Height correlation functions (HHCFs), H(r), in the X and Y directions and the 2D auto-correlation function were calculated from the AFM scans using the Gwyddion software (version 2.40), after levelling the surface. The HHCFs along the X and Y directions were calculated from different AFM scans in such a way that the fast scan axis was always aligned with the corresponding direction.

Tribological behaviour was evaluated using an in house pin-on-disk tribometer. The 100Cr6 steel balls were used as counterpart. The coatings were tested at two different temperatures at room temperature (approx. 23 °C with a relative humidity RH 35%) and 100 °C. The 100 °C was achieved by using two hot air guns pointed to the sample with the control of the temperature by a thermocouple placed near the coatings surface. The linear speed was set at 0.1 m/s. The normal load applied for the tests was 5 N, at room temperature the test duration was limited to 20,000 laps. However, in the cases where the wear track was very shallow, i.e. difficult to measure, the test duration was extend to 100,000 laps. At 100 °C the test duration was shorten to 10,000 laps.

3. Results and discussion

3.1. *Coatings chemical composition, morphological and structural characterization*

The coatings chemical composition and morphology were evaluated by EDS and SEM respectively. The elemental composition, thickness and deposition rate are presented in Table 2. All alloyed coatings presents a similar metal content in the range of 10–15 at. %. Although the coatings were deposited in the same deposition chamber, slightly different conditions were used to obtain the desired compositions as presented in Table 1. The DLCW and DLCAg coatings were deposited with an additional target of carbon with W or Ag pellets, respectively. These conditions were set based on previous work [17], although in the case of Ag pellets, it was necessary to reduce the number of Ag pellets due to the its higher sputtering yield. The DLCW coating present the highest deposition rate. This is mainly related with the highest power applied in the target with the W pellets. The lower deposition rate was observed for the pure DLC since only two C targets were used to deposit the coating. The deposition of the others coatings present similar deposition rates, once the power applied on the target used to alloy the coating with metal were identical. The selection of a composite target (carbon target with pellets) or a full takes in consideration the sputtering yield of the element, the alloying content and the power that should be used in order to have a good control of the coatings composition.

Table 2
List of deposited coatings, elemental chemical composition, total thickness and deposition rate.

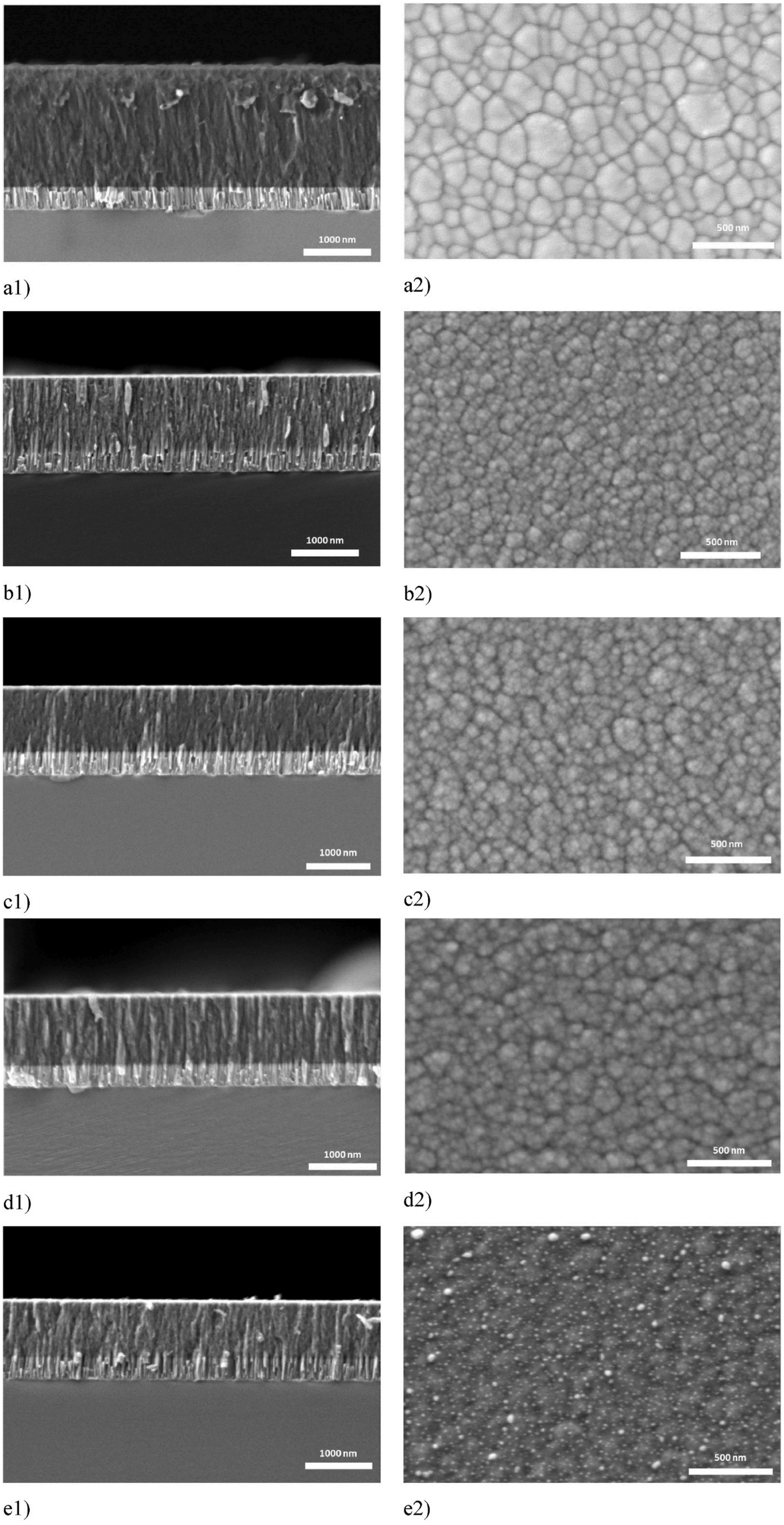
Coating	C (at. %)	O (at. %)	Ar (at. %)	Metal (W, Ag, Si)	Thickness (μm)	Deposition Rate (nm/ min.)
DLC	95.4	1.4	3.2	–	2.2	4.0
DLCW	82.2	0.8	2.7	14.3	1.4	14.3
DLCAg	82.9	1.8	3.0	12.3	1.2	6.1
DLCSi	82.1	0.8	3.0	14.1	1.4	6.2
DLCSiO	62.8	24.7	1.3	11.2	1.4	8.1

The coatings cross section and surface morphologies are shown in Fig. 1. All deposited coatings presents a very compact but columnar morphology. A Cr interlayer, with a thickness of approximately 300 nm, can be observed in Fig. 1 a1) to e1). The addition of alloying elements causes some changes in the coatings surface morphology as it can be observed in Fig. 1, a2) to e2). The pure DLC coating presents a surface morphology with well-defined borders corresponding to the end of the columns observed in the cross section morphology (Fig. 1 a2)). Similar surface morphology was observed for DLC coatings deposited by HIPIMS [31]. Alloyed DLCW, DLCSi, and DLCSiO coatings presents a typical cauliflower surface morphology (Fig. 1, b2), c2), d2)). The DLCAg coating presents an compact cauliflower morphology with bright dots on the surface (Fig. 1 e2)), corresponding to Ag clusters, in good agreement with to what was observed in other research works [6].

AFM scans of the coating's surface deposited on steel substrates are shown in Fig. 2. The same length scale of the height was used for the line scan representative of the surface topography, although, the maximum value labelled in each scan can be different. The coating with the highest surface roughness is the pure DLC, while, the lowest value was obtained for the DLCSi coating, as shown in Table 3. Taking in consideration the depositions conditions used in this work, it seems that the two main factors influencing the surface topography are the alloying elements and the coating thickness. The substrate bias is another of the deposition parameters that can also influence the surface topography, since it influences the energy of the ionised particles that are bombarding the growing film. However, in this case, although different bias voltage were used −110V (DLC, DLCW, and DLCAg) and −50V (DLCSi and DLCSiO) there is no significant difference based on the bias voltage even in coatings with similar thickness. Therefore, in this work, it's plausible to assume that the alloying elements are the main cause for differences of the surface topography. Indeed, it have been reported that this type of cauliflower type surface morphology is typical of unstable growth under surface diffusion limited conditions, where grains aggregate to form larger structures [32,33].

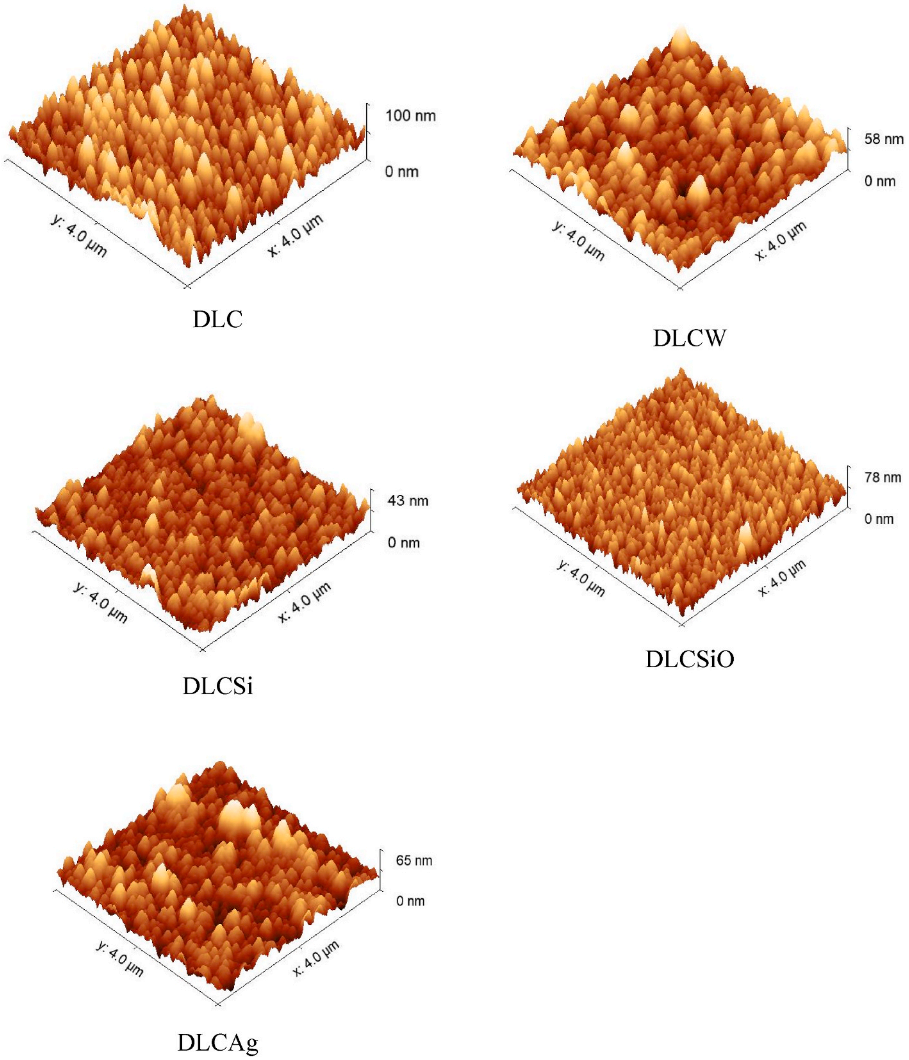
Raman spectroscopy can bring information about the influence of the alloying element on the bonding structure. The analysis is based on the evolution of the of the I_D/I_G ratio, the G-peak position and the G-peak FWHM

for the different alloying elements, as shown in Fig. 3. The lowest I_D/I_G ratio was observed for the pure DLC coating while the highest value was obtained for DLCSiO (see Fig. 3 a)). According with A. Ferrari [34] an increase of the I_D/I_G ratio is a result on a decrease of the sp^3/sp^2 ratio,



a1) a2) b1) b2) c1) c2) d1) d2) e1) e2)

Fig. 1. SEM images of the cross-section and surface a1) a2) DLC, b1) b2) DLCW, c1) c2) DLCSi, d1) d2) DLCSiO, e1) e2) DLCAg respectively.



DLC

DLCW

DLCSi

DLCSiO

DLCAg

Fig. 2. AFM surface topography of the coatings deposited on steel substrated, left side 3D image of the coatings surface topography right side surfce profile representative of the coatings topography of the analised area.

Table 3
Mechanical properties, Hardness reduced Young's modulus measured by nanoindentation.

Coating	Roughness RMS (Sq) (nm)	Hardness (GPa)	Reduced Young's modulus (GPa)
DLC	12.7	23.3 ± 1.9	219.0 ± 9.1
DLCW	7.5	16.1 ± 1.3	190.0 ± 8.3
DLCAg	8.1	11.5 ± 0.8	121.2 ± 3.2
DLCSi	4.4	17.7 ± 1.0	190.3 ± 4.7
DLCSiO	8.2	11.2 ± 0.6	128.8 ± 3.6

therefore, Si and O additions led to an increase of the sp^2 type bonds on the coating. This was also observed for the rest of the alloyed coatings. The pure DLC presents the highest G-peak FWHM (see Fig. 3c)). According with *W.G. Cui* et al. [35] for H-free DLC coatings an increase of the G-peak FWHM is related with the increase of the sp^3, therefore from the coatings deposited for this work we can assume from the Raman analysis that the pure DLC coatings has the highest sp^3 content. This corroborates the I_D/I_G ratio results.

The values of the Hardness - H and reduced Young's Modulus - E of the different coatings are presented in Table 3. The highest values of H and E were obtained for the pure DLC coating. One important feature of the DLC coatings is that it can present a wide range of properties depending on the deposition conditions used. For instance the variation of the bias voltage from floating to −100V results in a variation of the hardness from 8 to 22 GPa [36], also there are other deposition parameters that influence the coatings properties. From the alloyed DLC coatings, with elements that are carbide formers (Si, W) the hardness is lower than for pure DLC. This seems to be an unexpected result since higher hardness would be expected. The hardness of DLC type coatings is mainly dependent of morphology, structure and binding energy of the carbon atoms, where is normally accepted that a higher sp^3/sp^2 ratio results in higher hardness and Young's modulus [37]. Thus, since the level of SP^3 bonds on the coatings decreased with alloying elements the lower hardness of the alloyed coatings as compared to pure DLC is attributed to the decrease of the SP^3 type bonds as revealed Raman analysis. The lowest values of hardness were obtained with the coatings doped with Ag, and Si with O, in good agreement with the lower level of Sp3 bonds on the coating as suggested Raman analysis.

3.2. *Coatings tribological behaviour*

The coatings tribological performance was studied against steel balls at two different temperatures (room temperature – RT and 100 °C – HT). The interaction of the coatings against the counterpart is shown/discussed below.

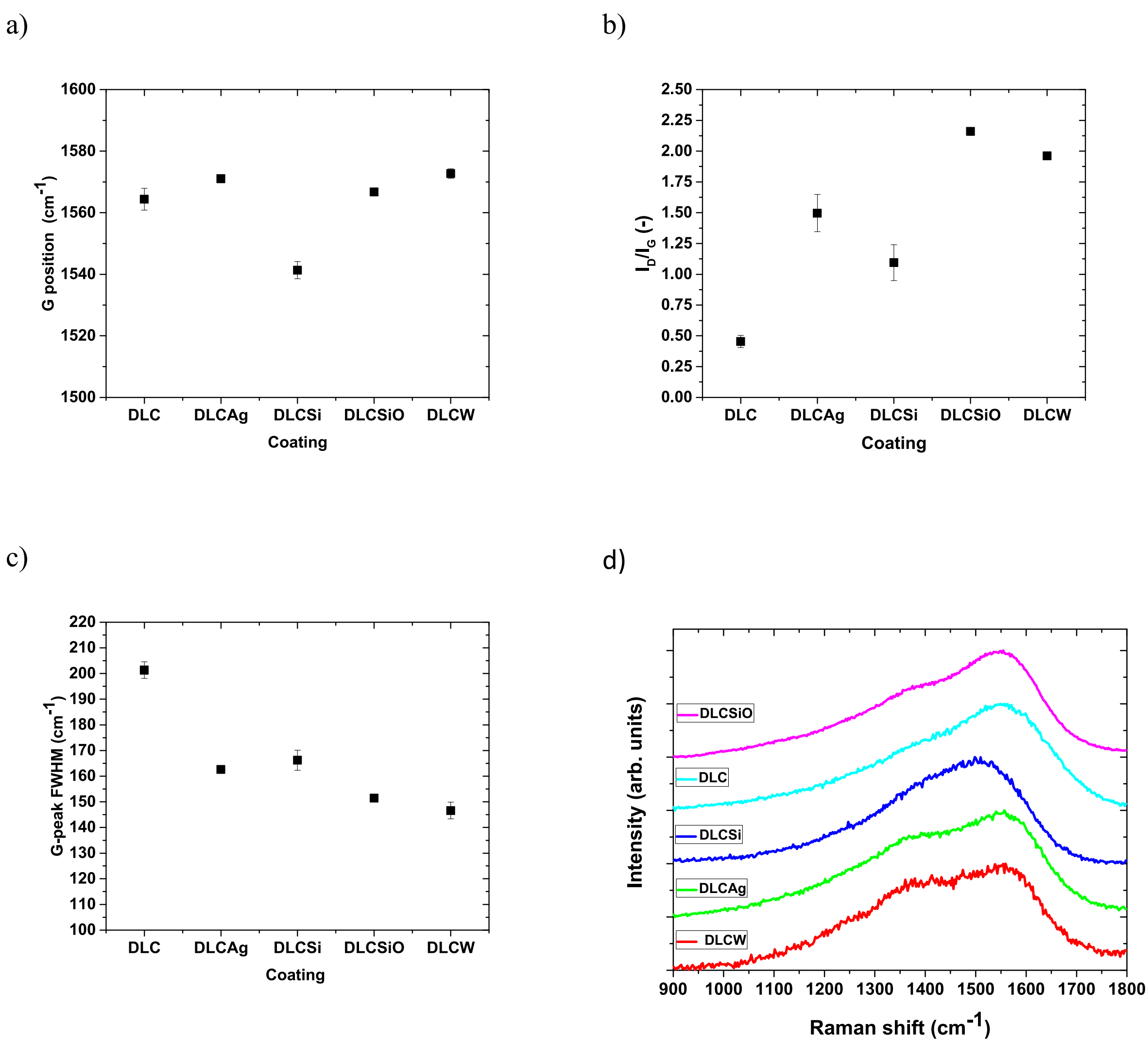


Fig. 3. Raman analysis of the coatings; a) G-peak position, b) I_D/I_G ratio, c) G-peak FWHM, d) Raman spectra for all coatings.

3.2.1. Friction coefficient

The evolution of the coefficient of friction during the tests at RT is shown in Fig. 4 a), whilst, at HT are shown in Fig. 4 b). At RT, the DLC, DLCSi and DLCSiO presented a stable COF level during all the test duration, while, the others two (DLCAg and DLCW) shown fluctuations of the friction during the tests, with significant variations for the DLCW coating. In the case of the DLCW coating, the variation on the COF has been reported to be caused by the continuous alternation between the formation and disruption of the tribolayer formed on the contact. At 100 °C, the DLC coating displayed an unstable COF. The DLC-W coating displayed a long running-in period, where after 400 cycles the COF stabilizes to ~0.76. All the other coatings displayed a uniform COF value during the entire test duration (see Fig. 5).

The COF average values of the coatings at room and high (100 °C) temperature are presented in Fig. 4c). The reference DLC coating displayed a COF value of ~0.15 as expected this value is in the range of the values reported in the literature for pure DLC coatings, which is attributed to the formation of a low friction graphite-like tribolayer in the contact. DLCW coating displayed the highest COF (0.43) among all the films. DLCAg coating displayed an intermediary COF value (0.23) between the DLC and DLC-W coatings, whilst, the DLC-Si and DLCSiO displayed the lower COF values in the range of 0.12–0.09. In the case of DLC coatings alloyed with Si, according with some authors [12], the formation of a silicon oxide layer at the sliding surfaces is the responsible for the low COF values observed. The increase of the temperature influences the COF values in two different ways, in the case of the pure DLC and DLCW coatings there is an increase of the friction with the increase of the temperature, while, in the other coatings there is a small decrease of the values. There are several factors which contribute to the coatings friction behaviour. For non-hydrogenated DLC coatings the presence of moisture is well known to contribute to the reduction of COF [27,38], therefore, the increase of the friction with the increase of the temperature to 100 °C is mainly related to the removal of the moisture from the sliding surfaces. Indeed, the lack of humidity, will not passivate the dangling carbon bonds and will not minimize C–C interactions of the free C particles, therefore, C will not provide low COF. For the alloyed coatings another factors can also contribute significantly to the friction behaviour, mainly the type of tribolayer formed. Further discussion will follow in subsection 3.2.3.

3.2.2. Specific wear rate of coatings

The specific wear rate of the tribological system was evaluated by mechanical profilometry and optical microscopy for the coatings and sliding counterparts, respectively (see Fig. 6). At room temperature DLC and the DLCW coatings presented the lowest wear rates. With 20.000 laps it was not possible to measure the wear crater, and therefore, the length of the tests were extend to 100.000 laps to produce measurable wear. The coatings that presented the highest wear rate were the DLCSi and DLCSiO, despite of their lower COF value. The increase of temperature to 100 °C result in an increase of the wear for all coatings in

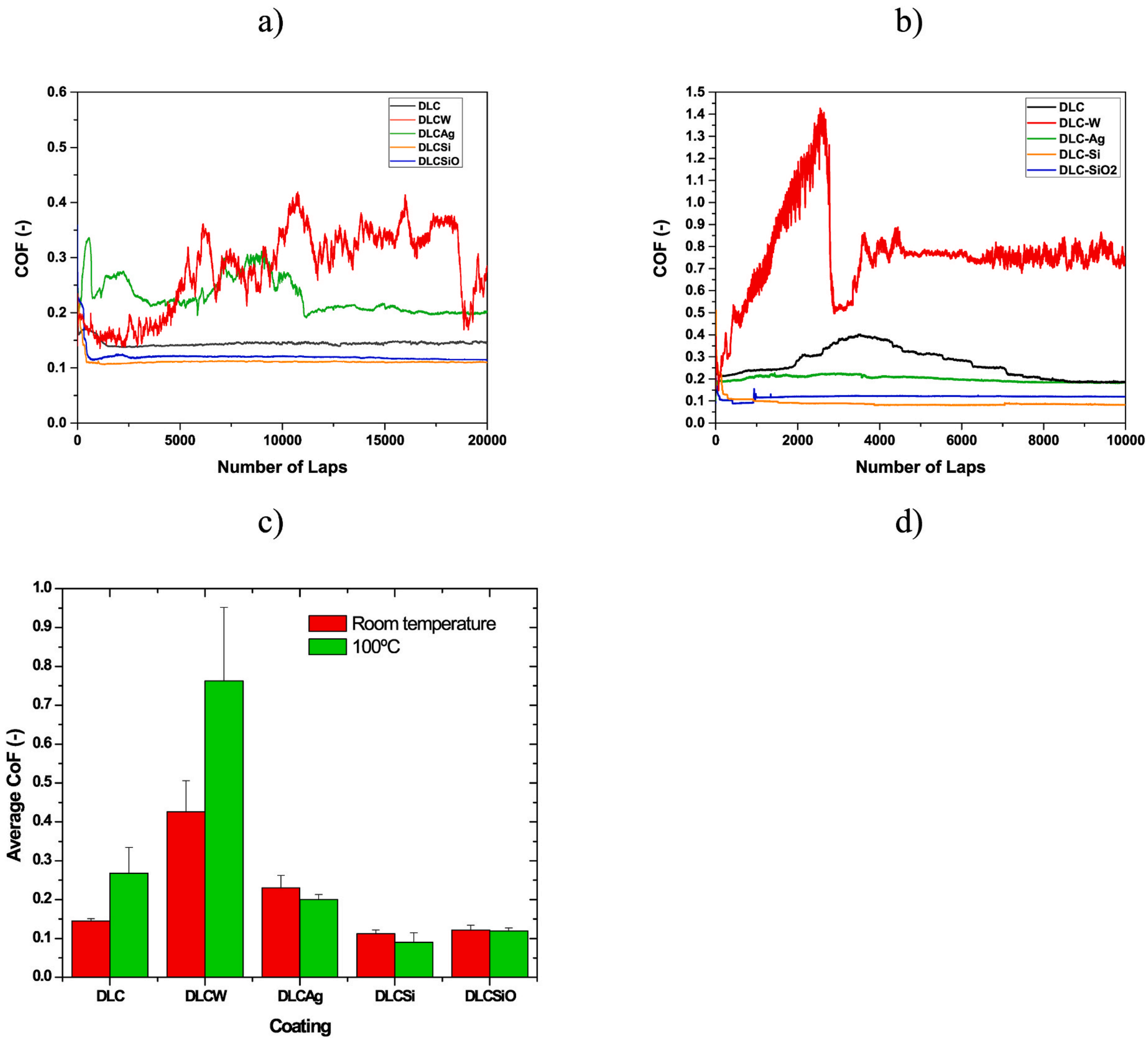


Fig. 4. Tribological characterization friction behaviour of pin-on-disk tests with steel balls: a) friction curves at room temperature for all coatings; b) friction curves for all coatings when tested at 100 °C; c) average friction for all coatings at room and 100 °C.

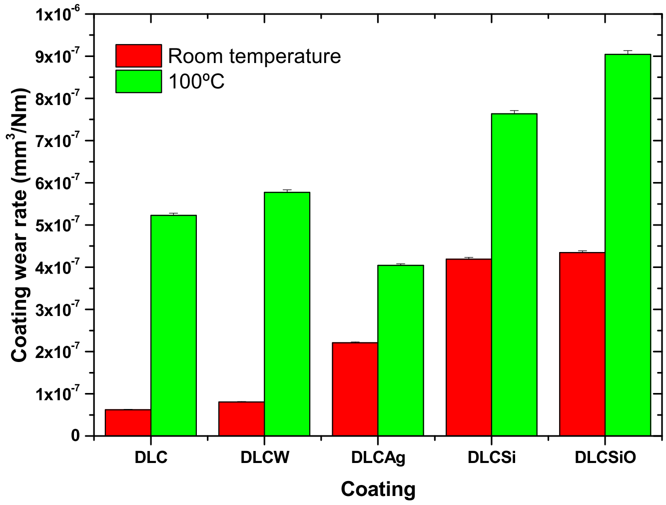


Fig. 5. Specific wear rate at room temperature and 100 °C of coatings tribological tested against steel balls.

relation to the tests performed at RT. This is an expected result, since softening of the films with temperature, provides easier removal of the material. The removal of the humidity also contributes to the increase of the wear. Without humidity more the dangling bonds are available to interact with the sliding partner resulting in an increase of the wear.

At 100 °C the coating that presented the lowest wear was the DLCAg, while, again the DLCSi and DLCSiO coatings are the ones with the highest wear, even despite of their low COF values as compared to the other coatings. As it will be discussed latter the lower wear observed for the DLCAg coating is be attributed to the formation of a well adherent transfer film on the steel ball (Fig. 7), due to the presence of Ag, which is well known for their ability to easy deform, leads to lower specific wear rate. DLC and DLCW coatings displayed a wear rate value in between the previous described coatings. Nevertheless, the specific wear rate is slight higher for DLCW coating as compared to DLC reference one.

The differences in the COF and specific wear rate values described above are influenced by many factors, including the coatings physical properties and wear mechanisms presented in the sliding contact. Thus, in order to explain those behaviours the interaction between the film and the counterpart was investigated and the main type wear mechanisms identified.

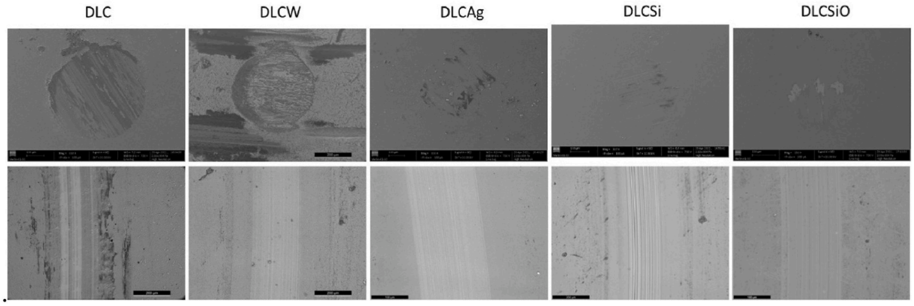


Fig. 6. Images of the steel balls and wear tracks tested at RT.

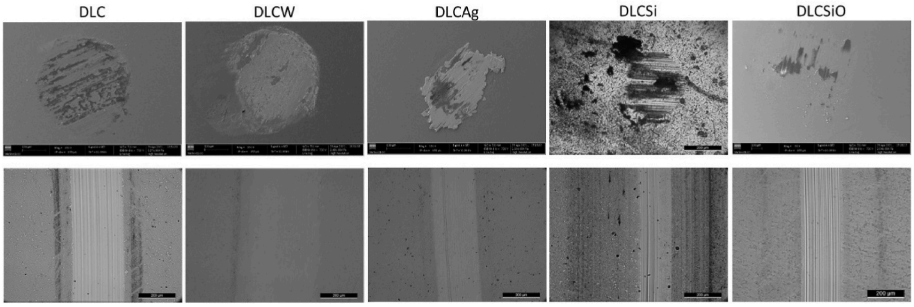


Fig. 7. Images of the steel balls and wear tracks tested at 100 °C.

3.2.3. *Wear mechanisms and surface analysis of the wear track*

After the tests, the wear mechanism and the transfer layer formed on the sliding ball was observed/characterized by optical microscope and SEM-EDS. The wear tracks and counterparts aspect after tribological tests at RT are displayed in Fig. 6, at RT the DLC reference coating showed adhered material either in the wear track and counterpart. The wear mechanism taking place is a mixture between adhesion and abrasion wear. According to the EDS analysis conducted at the ball wear debris (see Fig. S1 in supplementary material) the transfer layer is composed mainly by Fe, O and some C. From the three different spots analysed, spot 1 corresponds to the approximately to the composition of the steel ball with low O content, the others corresponds to the transfer layer with a significant amounts of oxygen and iron. Therefore, the worn material will be composed by iron oxide and some carbon from the coating. Thus the low friction coefficient of this coating can be explained by the presence of C in the transfer layer. Indeed, according to the literature, the lubricity was due to the presence of atmospheric humidity, which dissociates to H and OH, passivating the dangling carbon bonds and minimizing C–C interactions between the layers and the sliding interface. This combined with the high hardness of the coating will lead to a lower specific wear rate. However, hard Fe–O oxides which are adhered to the ball can be dragged in the wear track, producing grooves as displayed Fig. 6.

In the case of DLC-W coating similar amount of wear debris can be seen adhered to the ball counterpart, however, only abrasion type wear mechanism can be seen in the wear track. According to the EDS analysis the main elements taking place in the transfer layer are C, W, Fe and O, suggesting the presence of C, W–O, W–C and Fe–O compounds. Beyond the presence of C, as for the pure DLC coating, the presence of W–O would be expected to provide lubrication due to their recognized lubricious properties at high temperatures [39]. However, at this temperature their efficiency in providing lubrication is low as at such temperature the oxide is not easy to deform. On the other hand, the presence of W–C in the tribolayer adhered to the ball will scratch the surface promoting abrasive type wear mechanism. Thus the higher COF value of this coating can be attributed to the: i) less amount of C present in the tribolayer, ii) presence of W–O which is not so efficient in providing lubrication at RT conditions, iii) change of wear mechanism promoted by the presence of W–C adhered at the ball surface. This together with the lower hardness of the film as compared to pure DLC reference one leads to a slight increase of wear rate. According to Pu et al. [40] who studied the influence of W addition on the tribological performance of a DLC, the increase of W on the films leads to the increase of WC1-x phases in the contact, which act as hard abrasive particles accelerating the coating degradation and consequently wear rates. Additionally, the strong variation visible in the COF curve have been attributed to the continuous formation and destruction of the tribolayer during tests.

In the case of the DLCAg coating the transfer layer on the sliding ball is composed mainly by Ag, C, with some oxygen (see Fig. S2 in supplementary material). From the analysis it possible to conclude that the transfer layer can be composed by silver, carbon and some oxides. Polishing wear is the type of wear mechanism taking place in the wear track. Despite of the well know low friction properties of Ag in sliding contacts, the COF values of Ag at RT are higher than for pure DLC coatings, since at RT Ag is not easy to slip. This together with the lower amount of C in the contact justifies the higher COF value. Combining this with the lower hardness of this coating (even lower than for DLC-W) lead to a much higher specific wear rate value.

In the case of the Si and SiO containing coatings, the transfer layer on the sliding ball is mainly rich in C, Si and O rich. According to the previous study of the current authors, based in XPS analysis, those wear debris are C, Si–O and SiC phases. The wear track of the films displayed similar severe abrasion wear mechanism. Thus, the low COF of the current coatings can be explained by the combined effect of presence of C in the tribolayer, like in pure DLC coating, and presence of Si–O which is also known to provide low COF values [12,13]. Despite of the low friction properties of those films, their specific wear rate is much higher than in the other coatings. This can be explained by the presence of SiC stick at the ball surface. The presence of hard particles of SiC stick at the ball counterpart leads to a severe abrasion of the film surface and consequently to higher specific wear rates. It is also expected that the tribolayer of the DLCSi coating is much richer in SiC phase than DLCSiO film, as in the latter case during deposition the formation of Si–O is achieved [13]. Therefore a higher specific wear rate would be expected for the former film, which contradicts the current results, where similar specific wear rates were reached. The similar specific wear rates results can be attributed to the higher hardness of the DLCSi coating which even despite of the higher amount of SiC expected in the tribolayer will resist more to wear.

At 100 °C an increase of the specific wear rate is observed for all the coatings. This can be attributed to the softening of the films with temperature and the removal of the moisture form the sliding surfaces, which provides easier removal of the coatings and increases the interactions between the sliding bodies, respectively [17,30]. Similarly to RT tests DLC reference coating tested at 100 °C displays adhere material to the counterpart. However, only abrasive type wear mechanism is observed in the wear track. EDS analysis revealed that the wear debris are C and Fe–O rich. In the DLCW coating the counterpart is fully covered by wear debris, which similarly to room temperature the EDS analysis revealed to be C, W–O, W–C and Fe–O phases, however, the amount of W–O increased due to the easier oxidation of W–C phase promoted by the increase of temperature. The wear track is smooth with polishing wear type wear mechanism. In both coatings the COF values increased in relation to the RT values. This can be explained by the absence of humidity, which will not passivate the dangling carbon bonds and will not minimize C–C interactions of the free C particles, thus, giving rise to high friction values. Despite of the high amount of WO in the tribolayer of the DLCW coating, at this temperature their lubricious effect is not effective since is not easy to deform and consequently provide low friction. The presence of W–C particles adhered to the counterpart will damage the film surface as in RT tests, promoting polishing wear mechanism.

The counterpart of the DLCAg coating is fully covered with adherent wear debris. EDS analysis revealed that the phase is mainly formed by Ag. The Ag as soft metal is easier to deform as compared to RT temperature condition, promoting a slight decrease in COF as compared to RT tests. Even despite of the lower hardness of this film as compared to DLC and DLCW coatings, and the further coating softening with temperature, the specific wear is lower among all the coatings since the interaction of Ag adhered at the counterpart with the film wear track, protects the coating from wear. It should be highlight that even the wear of the counterpart is very low as can be seen in Fig. 7.

In the case of DLCSi and DLCSiO coatings similar wear debris, as detected at RT, are adhered to the ball counterpart. However, high amount of Si–O is expected in relation to SiC due to the easier oxidation of the latter phase at 100 °C. This may be the cause for the slight decrease of friction of these coatings at 100 °C. Despite of the lubricious effect provided by SiO on the contact, the softening of the coatings at this temperature and the presence of hard SiC particles leads to the severe abrasion of the coating surface (see wear mechanism in Fig. 7) and consequently to the higher specific wear rates among all the coatings.

In summary, it was observed that COF and wear specific wear rate are not directly related, and the third bodies formed on the sliding surfaces have major influence on the tribological performance of the system.

4. Conclusions

In this work DLC coatings were deposited by DCMS magnetron sputtering and alloyed with different elements, W, Ag, Si and Si–O. Alloying the coatings reduces the mechanical properties, hardness and Young's modulus due the decreased of the sp^3 content as supported by the Raman spectroscopy analysis.

The tribological behaviour of the coatings was assessed against steel balls at two different temperatures (room temperature and 100 °C). The results concerning the wear performance at room temperature showed that the DLC reference coating displayed the lower specific wear rate. This results is attributed to the combined effect of higher hardness with the presence of a humid atmosphere which dissociates to H and OH, passivating the dangling carbon bonds and minimizing C–C interactions between the layers and the sliding interface, thus decreasing COF and wear rate. DLCSi and DLCSiO coatings which displayed the lowest COF values at RT, showed the highest specific wear rate. This is caused by the stick of SiC hard particles at the ball counterpart which promotes severe abrasion of the films surface. With the increase of the test temperature to 100 °C all coatings registered an increase of the specific wear rate, with more impact in the coatings with the best wear resistance at room temperature. This was attributed to the combined effect of i) absence of humidity, which will not passivate the dangling carbon bonds and will not minimize C–C interactions of the free C particles, and ii) softening of the film with the temperature, which leads to easier removal of the material. Two different behaviours were observed on the COF values at this temperature: for DLC and DLCW coatings a significant increase of the friction was observed, whilst for the other coatings a slight decrease of the COF values is observed. Therefore for this coatings moisture in the environment has minor role in the friction behaviour, thus the oxides in the tribolayer contributes to the low COF values of the coatings as compared to DLD and DLCW coatings.

Thus, it can be said that for DLC doped coatings the COF values an and wear are not directly related, and the third bodies formed on the sliding surfaces have major influence on the tribological performance of the system.

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. Supplementary data

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