Author's Accepted Manuscript

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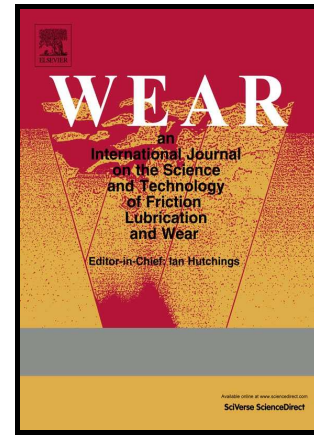
Cite this article as: A.H.S. Bueno, J. Solis, H. Zhao, C. Wang, T.A. Simões, M. Bryant and A. Neville, Tribocorrosion evaluation of hydrogenated and silicon DLC coatings on carbon steel for use in valves, pistons and pumps in oil and gas industry, *Wear,* https://doi.org/10.1016/j.wear.2017.09.026

Tribocorrosion evaluation of hydrogenated and silicon DLC coatings on carbon steel for use in valves, pistons and pumps in oil and gas industry

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Abstract

Several components in the oil and gas industry are subjected to wear and corrosion. This work evaluated the feasibility of using Diamond-Like Carbon (DLC) coatings in Subsea Safety Control Valves (SSCV), piston and pumps. These are made from API X65 carbon steel and are subjected to wear and corrosive/saline environments. Coatings were deposited using Plasma Enhanced Chemical Vapour Deposition (PECVD). The electrochemical behaviour of Silicon-doped and Hydrogenated DLC films was evaluated before and after wear tests. Film characterisation included nano-indentation, surface roughness, micro-abrasion testing, Raman spectroscopy, atomic force microscopy and scanning electron microscopy. Electrochemical tests and electrochemical impedance was also measured. Sliding wear tests against silicon nitride were conducted with a maximum initial Hertz stress of 150 and 400 MPa under dry and wet conditions. The H-DLC had better wear performance than Si-DLC. The advantages of H-DLC were related to higher hardness increasing the wear resistance; small galvanic coupling between DLC and steel, inhibiting the localised corrosion into the DLC defects; lowest anodic current, suggesting high resistivity to use as a corrosion barrier for steel and the corrosion process on the substrate that did not affect DLC properties (adhesion and wear/ corrosion resistance).

1 – Introduction

The recent interest and great challenges for oil and gas companies are to improve the efficiency and viability of crude oil recovery. However, there are some barriers related to the viability for commercial extraction, such as the water/ oil that contains high salinity and sand particles. Therefore, DLC films can be a good candidate for protection of carbon steel used in critical equipment of oil transportation that need to preserve its structural integrity. For example, Subsea Safety Control Valves (SSCV), pistons and pumps. DLC coatings could improve the oil carriage by reducing friction, wear and corrosion inside the pipelines and their components.

Currently, the main methods used to avoid internal scale corrosion are inhibitors due to the fact that they promote adsorption of films on the surface, and as a result, enhance the corrosion resistance by forming a compact protective layer [1–3]. However, there are a number of conditions that can affect the efficiency of these inhibitors, such as fluid (composition, temperature, flow velocities, pressure of CO_2 gas, wettability of the fluid, fluid density and types of crude oil), solid particles (sand contents, size, attack angle of the particles, density and velocity) and steel (hardness, microstructure, strength, ductility and toughness) [1,2]. Seamless steels coated with resin are used to improve the wear and corrosion resistance in pipelines and drills [4]. However, polymeric coatings lack hardness and can be degraded. Because of this, DLC coatings could be applied on internal parts of pipelines providing good corrosion resistance for oil and gas applications [5,6].

DLC coatings are designed to have a combined resistance to wear and corrosion in automotive and biomedical areas [7–13]. However, DLC has not been widely studied and used in some parts of the crude oil exploration, such as SSCV, pistons and pumps. For the above reason, the study to evaluate the feasibility of using this coating for surface modification of carbon steel is very interesting for the oil and gas corporations.

The properties of DLC could improve the efficiency for the transport of oil by reducing the friction, wear and corrosion inside the equipment [3], such as: amorphous and inertness structure, hydrophobic, low coefficient of friction (CoF), high corrosion resistance, high hardness, high Young`s modulus and good wear/abrasion resistance [7–10,14–16]. Then, PECVD could be a good option to create an internal scale corrosion barrier for a carbon steel to avoiding the precipitation of salt scales. However, the main

results in the literature are associated with defects and microstructure. Only few papers have been postulated to corrosion resistance for DLC coatings [1,2,5,14,17].

Manhabosco et al. [10] reports that the main problem for DLC coatings is associated with failure and delamination of the film. Defects are related to poor adhesion of the film, plastic deformation of the bulk material and cracking on the surface coating, which could be linked to chemical and mechanical properties between the film and substrate [18]. Therefore, adhesion layers and surface treatments are being studied to improve the mechanical properties, like load bearing capacity, hardness and tension distribution between the film and bulk material. According to Hadinata et al. [17], there is an extremely high mechanical resistance in DLC coatings mainly associated with wear/corrosion resistance, despite some electrochemical parameters involved in the process were not completely explained.

There are several studies related to tribocorrosion of stainless steel coated with a-C:H films. However, literature reporting the combined effect of the tribological conditions in a corrosive medium for a-C:H and a-C:H:Si using carbon steel as a substrate is scarce [1,2,5,7–9,14,17]. The behaviour of these materials subjected to tribocorrosion can be very complex owing to many parameters involved in the process, but sliding testing simultaneously with the use of electrochemical techniques could contribute to better understand the deterioration effect that takes place.

In this work, the tribological and electrochemical performance of two different functional layers on carbon steel was studied, namely amorphous hydrogenated DLC and silicon doped DLC.

2 – Experimental details

2.1 – Materials

The H-DLC and Si-DLC coatings were deposited on API X65 carbon steel discs of dimensions 25 mm in diameter and 6 mm in thickness. The substrates were mechanically polished using 1 μm diamond paste with a maximum roughness of $R_a = 0.08$ μm. After polishing, the specimens were ultrasonically cleaned in acetone (10 min) followed by rinsing in deionised water and dried in air jet. The substrates were first

cleaned inside the chamber with sputter-etch in argon prior to any deposition. The coatings were produced using the PECVD technology, and the C_2H_2 gas was selected for the reaction gases at a pressure of 0.3 Pa. The substrate was maintained at the temperature of less than 200 °C, the pulsed bias was a voltage of 780 V with a frequency of 40 kHz for the plasma. The deposition rate was about 0.8 µm min^{-1} for hydrogenated DLC and 0.6 µm min^{-1} for Si-DLC. The deposition time is about 126 minutes for the interlayer and 138 minutes for the DLC films. The deposition procedure included an adherent Cr interlayer (by DC magnetron sputtering) followed by the DLC coating, namely, Cr/WC/a-C:H, with 20-40 at. % of H content and Si-DLC.

2.2 – Characterisation of the DLC coatings

The roughness of surfaces was evaluated using two-dimensional contacting profilometry (Talysurf5, Taylor-Hobson, UK). Surface roughness data of 8 mm trace was analysed to the least square line, with Gaussian filter, 0.25 mm upper cut-off and bandwidth 100 ± 1.

The hardness and elastic modulus values were measured by depth-sensing Nano indentation (MicroMaterials, Wrexham UK). The diamond indenter was a Berkovich tip. The load was incremental with depth from 1 to 100 mN and a matrix of 50 indents was used. The maximum penetration was of 10% of the film thickness to avoid the influence of substrate.

Atomic Force Microscopy (AFM, Bruker, ICON dimension with scan assist) was used to analyse the surface topography before and after tribology tests (outside and inside the wear scar). The surfaces were cleaned with acetone before analyses. The scan images were obtained using a silicon tip (cantilever stiffness ~0.4 N/m and tip radius of ~10 nm) in contact mode and a scan area of 10 μm x 10 μm.

A Renishaw Raman spectrometer was used to characterise the bonding structure of the DLC films. The extended and static modes were used to detect chemical compound formation and the carbon peaks (disorder D and amorphous graphitic G peaks), both for the coating structure before and after wear tests. All measurements were carried out in air at room temperature (20 ±2 °C), 35-50% RH, with a wavelength of 488 nm and 2 mW power. Data was fitted with a Gaussian Line shape to show the G and D peaks positions and the ratio of peak intensities. The I_D/I_G ratio was considered as an indicator of the carbon sp^2/sp^3 structure. Curve fitting was done considering full-width at half-maximum (FWMH) as constraint.

Scanning Electron Microscopy (Zeiss EVO MA15 Variable Pressure and field emission SEM) was used to evaluate the surface morphology and cross section microstructure to examine the multilayers (adhesion and DLC layers), before and after wear tests. Assessment of the surface chemical composition and cross section of the coating was carried out with the energy dispersive spectroscopy (EDS). Hydrogen element ($Z = 1$) do not have characteristic X-rays and therefore it is not shown both in the corresponding EDX analysis and the composition profiles.

White light interferometry (NPFLEX Bruker) was employed after tribology test to determine the volume and area of the worn track. Optical microscopy (LEICA DM 6000M) was utilised to analyse the diameter of wear scars on the balls after tribology tests.

2.3 – Mechanical tests

The scratch test is an effective method to obtain critical load and to identify the beginning of failure along the film. The tests were carried out using progressive loads from 0.1 to 80 N with a load rate of 100 N/min and for a transverse scratch length of 8 mm in dry condition. The scratch tester was equipped with an acoustic emission monitoring sensor.

The tribological tests of H-DLC and Si-DLC were carried out with a ball-on-plate tribometer. The horizontal frictional force is measured by the load cell which is a piezo-electric transducer that converts the analogue signal into a digital one to be then processed by Labview software. Steel balls are often used as a counter body to study only tribology aspects [19]. However, tribocorrosion is the aim of this study, which uses more complex parameters to analyse. In this study, we simulate extreme wear conditions by using Si_3N_4 balls as high hardness counter body. These also own to have a good chemical stability and avoid galvanic coupling between both surfaces during tribocorrosion experiments. Ceramic balls used were composed by Si (62.0 wt.%) and N (37.5 wt.%) with a 12 mm diameter, 0.02 µm surface roughness and hardness of HV_{50g} 1600. These were used in a reciprocating movement against stationary DLC coated steel. The maximum Hertzian contact pressures (P_{max}) were of 150 MPa and 400 MPa for 6 h, at a frequency of 1 Hz, sliding velocity of 0.02 ms^{-1} and 10 mm sliding stroke. These contact pressures were defined to simulate real conditions where equipment for oil and gas can be subjected. The tests were carried out at room

temperature of 18-23 °C in dry condition with relative humidity approximately of 25% RH and in wet condition with a solution of 3.5% NaCl at pH 6.5.

2.4 - Electrochemical tests

A computer-controlled potentiostat (Solartron potentiostat/galvanostat) was used for the electrochemical tests. In this study two methods were used: Potentiodynamic and EIS. Potentiodynamic polarization curves. Anodic polarization curves, naturally aerated with scan rate of 30 mV/min and in a range from -1.8 V up to + 0,5 V, performed separately. Electrochemical impedance spectroscopy (EIS): Amplitude of 5 mV (Ag/AgCl/KCl) with the frequency of 30 kHz–10 MHz. For the polarization and impedance tests were carried out before and after the tribology tests with the solution of 3.5% NaCl, pH: 6.5 and at room temperature of 18-23 °C. Prior the tests, the samples were immersed in the solution for 30 min to stabilize the open circuit potential (OCP). The conventional three electrodes cell was used with an Ag/AgCl/KCl (Thermo Scientific) as reference and counter electrode, and DLC films as a working electrode.

3 – Results and discussion

3.1 Characterisation of DLC films

Figure 1 shows SEM backscattering images of adhesion layers of Cr/WC for H-DLC and Cr/WSi for Si-DLC; and EDS line scan spectra of cross sections. H-DLC (Figure 1a) exhibited a surface layers composed of iron (carbon steel), adhesion layers of Cr (1.7 μm), W (1 μm) and a final layer of H-DLC (2.7 μm). Si-DLC (Figure 1b) presented adhesion layers of Cr (1 μm), W (1 μm) and a final layer of Si-DLC (3 μm) The interface between both films and bulk material showed to be homogeneous all over the surface analysed and without the presence of defects. An interlayer of W was detected in both subtract. Literature [20,21] shows that the interlayer WC and H forms a non-stoichiometric hydrogenated tungsten carbide WC:H, also known as W-C:H or as W-DLC.
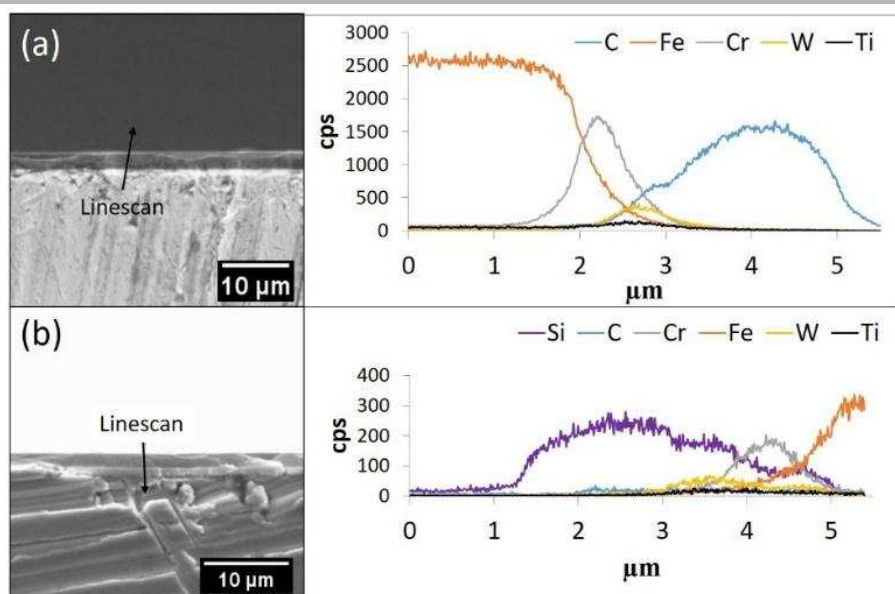
Figure 1. Backscattering SEM images of cross section and linear EDS scan of: (a) H-DLC and (b) Si-DLC films.

Literature [5,8,14,17,22] shows that the Raman spectrum of the coating has two types of C-C bonding structure, where diamond-like (sp^3 – D band) is found between 1200-1450 cm^{-1} and graphite-like structure (sp^2 – G band) between 1500 – 1700 cm^{-1}. Raman spectrum of DLC films before and after wear tests are presented in Figure 2, exhibiting D (Diamond-like) and G (Graphite-like) bands. Both DLC coatings showed peak of G higher than D, indicating graphite-like structure as predominant in both films. The spectrum of H-DLC (Figure 2a) shows D and G bands with peaks (Raman shifts) of 1365 cm^{-1} and 1549 cm^{-1}, respectively. Hence, the ratio of D and G peaks (I_D/I_G) was 0.42. Si-DLC (Figure 2c) spectra shows D and G bands with peaks of 1321 cm^{-1} and 1501 cm^{-1}, respectively and with ratio of D and G peaks as $I_D/I_G = 0.24$.
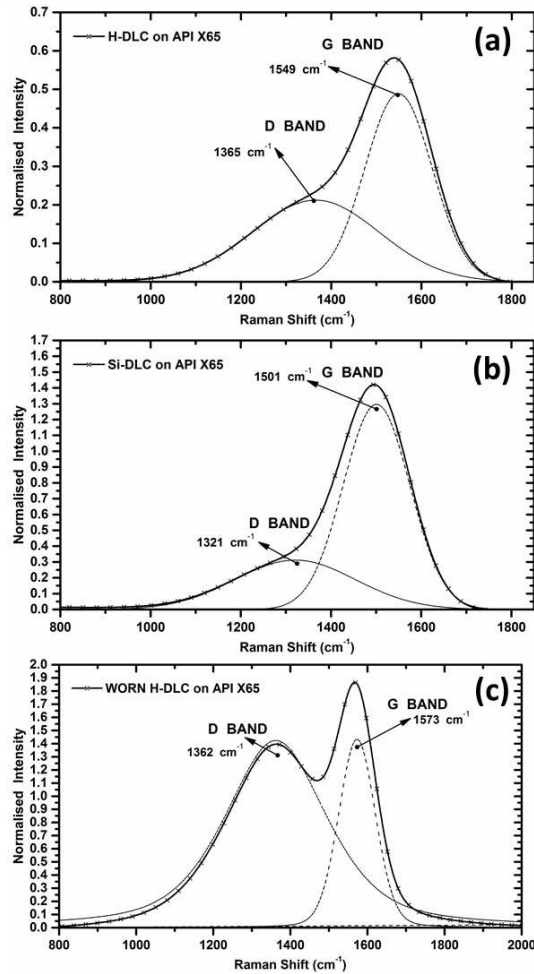
Figure 2. Raman spectra (a) H-DLC before wear test, (b) H-DLC after wear test and (c) Si-DLC before wear test.

AFM images of surface topography, before wear tests, are presented in Figure 3 a-b. H-DLC film (Figure 3a) shows a roughness surface containing large and small grains, compact and homogeneous. A maximum roughness (R_y) of 3.10 µm was obtained calculated from an area of 10x10 µm. The maximum roughness of H-DLC was 0.13 µm slightly smoother surface than Si-DLC (Figure 3a), with Ry = 0.27 µm, which also held large and small grains with compact and homogeneous characteristics.
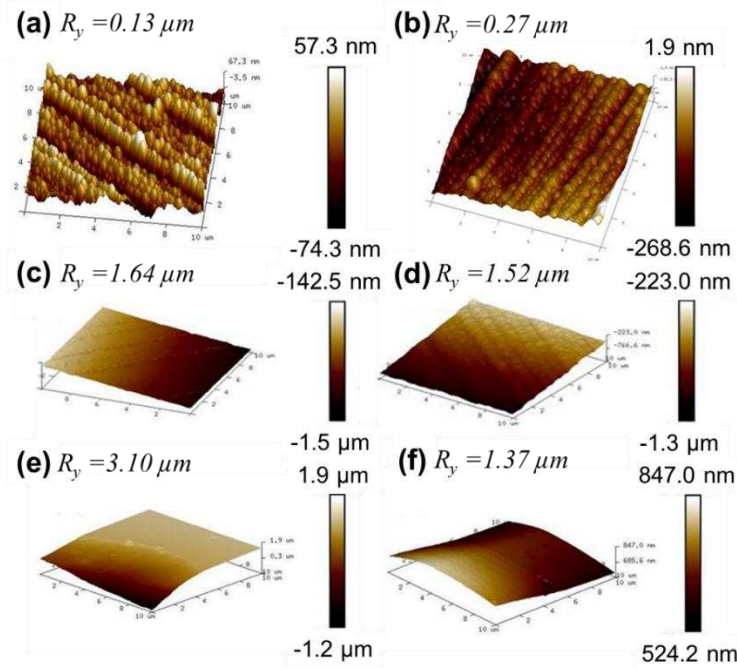
Figure 3. AFM images: (a) H-DLC before wear tests, (b) Si-DLC before wear tests, (c) H-DLC - Dry condition at contact pressures of 150 MPa, (d) H-DLC - Wet condition at contact pressures of 150 MPa, (e) H-DLC - Dry condition at contact pressures of 400 MPa and (f) H-DLC - Wet condition at contact pressures of 400 MPa

After wearing of the H-DLC surfaces, an increase of roughness was generally observed. This indicates that when the contact pressure increased, the plastic deformation of the surface asperities also increased. The samples under dry environment at 400 MPa (Figure 3 e) were the worst condition due to film delamination. Therefore, bits of H-DLC coating were emerged off the surface of API X65 carbon steel, as SEM images shows (see Figure 4c). The best lubricated conditions were shown to H-DLC coating under wet condition submitted to 150 MPa contact pressure. The results presented the lowest roughness change and surface degradation, as SEM EDS linescan detected very low variation of carbon across the wear track (see Figure 4b).

Figure 4. SEM secondary electron images and EDS linescan composition profiles of cross worn track for (a) H-DLC - Dry condition at contact pressure of 150 MPa, (b) H-DLC - Wet condition at contact pressure of 150 MPa, (c) H-DLC - Dry condition at contact pressure of 400 MPa, (d) H-DLC - Wet condition at contact pressure of 400 MPa and (e) Si-DLC - Dry condition at contact pressure of 150 MPa

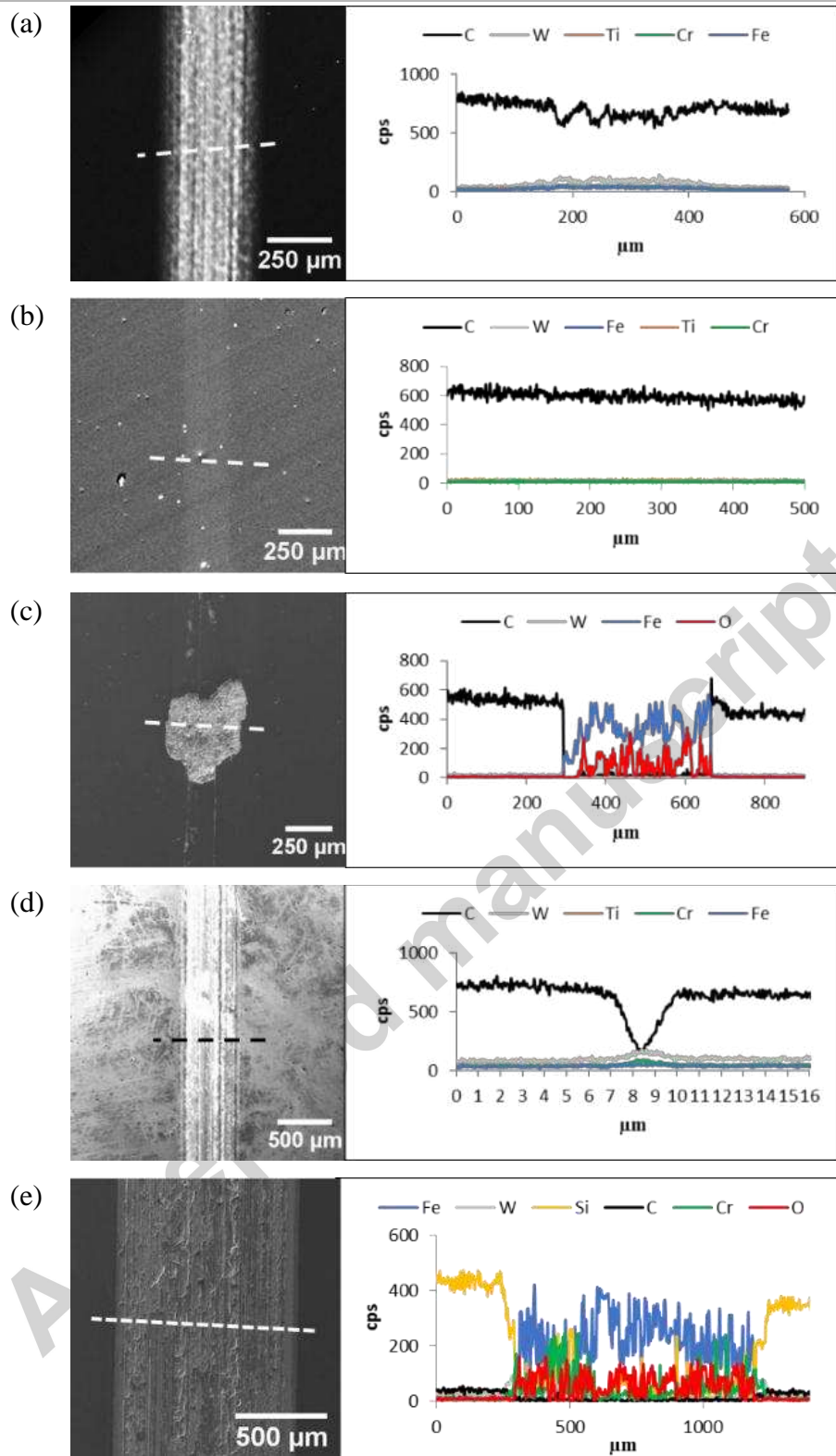The Si-DLC (Figure 4e) had the largest wear track and wear rate when compared to H-DLC which presented total delamination. It probably occurred because Si-DLC presented lower hardness than H-DLC, promoting less resistance to wear. Nano indentation results demonstrated hardness values of 20.4 and 14.1 GPa for H-DLC and Si-DLC, respectively. In addition, according to Jellesen et al. [23], the amount of sp^3 bonding and hydrogen are important to improve the hardness and wear properties. Thus, H-DLC presented more hardness and more wear resistance than Si-DLC.

The DLC film presents a meta-stable structure that is formed by an amorphous carbon with some crystalline phases and fractions of sp^3 and sp^2 bonds. The characteristics of the sp^3 bonds are associated with mechanical (hardness, rigidity, fracture toughness, wear and friction), chemical and electrochemical properties (corrosion resistance). In addition, the sp^2 controls the electronic properties [15].

Liu and Kwek [14] have shown that the formation of sp^3 bonds occurs when the bulk surface received the carbon ions in higher kinetic energy, which can be produced by increasing the pulse bias during the deposition process of the DLC film. Therefore, the kinetic energy of the carbon ion tends to increase when there is a high voltage applied on DLC film deposition process, causing the formation of diamond-like (sp^3 – D band) by the bombardment of carbon ions on the bulk surface. However, when there is a high value of bulk bias, a high energy of carbon ions, applied by a pulse bias above 500V, promotes the graphitization by the formation of a DLC film with graphitic clusters spread, causing a roughness on the surface of the DLC coating. This explains the results obtained in this work, i.e. since the DLC films were deposited at 780V, it presented high concentration of graphite-like structures (sp^2 – G band, Figure 2 a and c) and high roughness (observations through AFM, Figure 3 a and b).

3.2 Mechanical properties

H-DLC presented Young's modulus, hardness and roughness of 181.2± 7 GPa, 20.4 ± 3 GPa and 0.02 ± 0.005 µm. Si-DLC had 132.6 ± 9 GPa, 14.1 ± 4 GPa and 0.002 ± 0.0005 µm, respectively. The scratch tests on Si-DLC (Figure 5b) revealed good adhesion to carbon steel substrate with a critical load of 23 N of the incremental load (2.3 mm depth) with no signal of cracking. Point A (Figure 5b) indicates the onset of

angular cracks at the edge of the groove caused by a higher load of almost 40 N at the rear of the contact end but with no evidence of adhesive failure. The high amplitude of acoustic emission (AE) peaks at point B, namely, penetration depth of 4.8 mm and a load of 50, 31 N, are evidence of material activity and with the aid of the images, the presence of transverse semi-circular cracks in the bulk material can be observed. This situation is sustained until the test was completed. From all the above, it can be considered critical load > 23 N for the present coating without any interfacial fracture or adhesive failure. Unlike Si-DLC, the H-DLC coating revealed weaker coating resistance since the beginning of the test as shown in Figure 5a. From the evident small peaks, there is a possible premature failure which could be due to microscopic interfacial fractures with a critical load of 5.3 N. This behaviour could also be indicative of insufficient adhesion. However, as the indenter advances forward and penetration depth gradually increases with the scratch load and there is no evidence of flaking and/or delamination into the groove or by the edges of it. Therefore, it clearly establishes that H-DLC coating is less ductile than the Si-DLC. Thus, H-DLC presented better mechanical resistance, probably due to higher hardness. There was no evidence of adhesive failure.
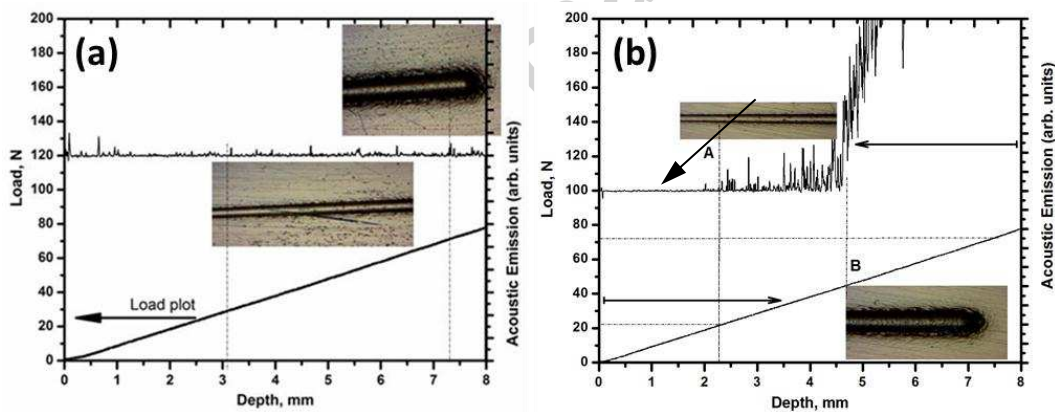

Figure 5. Scratch induced acoustic emission of the (a) H-DLC and (b) Si-DLC coatings.

Figure 6 shows the variation of coefficient of friction (CoF) with contact pressures of 150 e 400 MPa and in dry and wet conditions. A summary of CoF values at the end of sliding test are given in Table 1. H-DLC exhibited lower levels of CoF than Si-DLC for all test conditions.
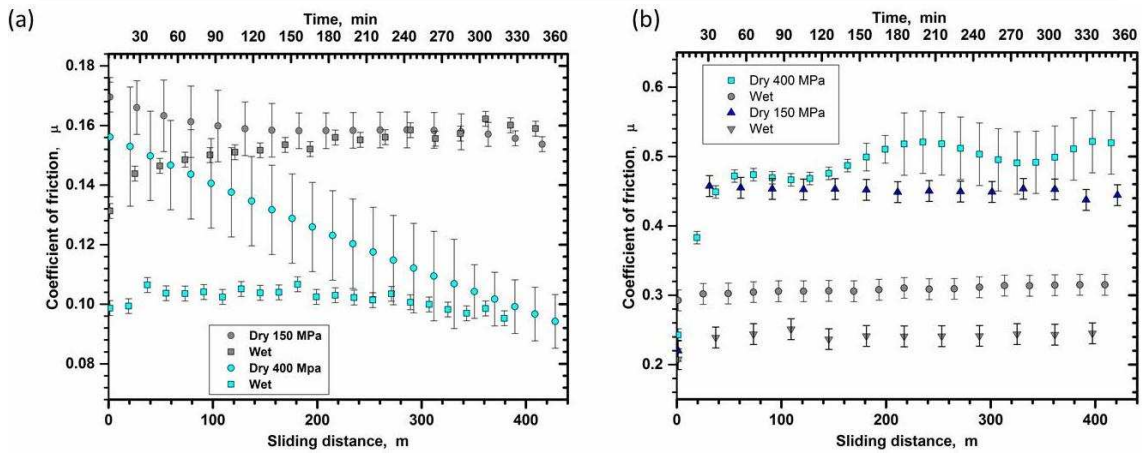
Figure 6. CoF curves under dry and wet conditions for (a) H-DLC and (b) Si-DLC

Table 1. Comparison of CoF at the end of rubbing test for H-DLC and Si-DLC

| Coating | Contact Pressure (Mpa) | | | |
| | 150 | | 400 | |
	Dry	Wet	Dry	Wet
H-DLC	0.16	0.15	0.10	0.09
Si-DLC	0.43	0.24	0.48	0.31

The highest CoF of Si-DLC occurred in dry conditions. Unlike the Si-DLC, a better adhesive strength was observed on the H-DLC, i.e. its surface did not undergo adhesive failure after the wear test under wet conditions at the lower contact pressures. This results are confirmed by SEM EDS linescan (Figure 4), in which carbon and silicon are the trace element that confirm the presence of H-DLC and Si-DLC coatings, respectively.

The borderline difference of CoF between Si-DLC results is associated with the solution, while for H-DLC the contact pressure played more important role. As shown in Figure 6 and Table 1, the H-DLC and Si-DLC coatings undergo a reduction in friction under wet conditions. The literature [24,25] describes that DLC films do not undergo elastic and plastic deformation under the metal substrate submitted to high loads. Therefore, lubricants are used to reduce the wear and friction on DLC films, such as ionic liquids that reduce the friction and increase the load carrying capacity. Based on this researches, it is evident that NaCl solution can also reduce the friction. However,

this solution is rather aggressive and capable of attacking the metal substrate at the localised defects in the coating.

H-DLC tested with a contact pressure of 400 MPa in dry conditions presented a decrease of CoF during test. According to Manhabosco et al. [10], such reduction is linked to the roughness and hardness of the H-DLC coating. The contact pressure is mostly concentrated at the top of the material crests when the sliding starts, and this small contact area induces higher shear stress.

The variation of CoF with sliding distance with respect to loading in H-DLC tested under both conditions, clearly shows a decrease in the steady state values of CoF when the contact pressure is augmented. In general, this reduction occurs when the contact pressure of some carbon layers of the H-DLC film are transferred to the ball creating a lubricious graphite-like or amorphised transfer layer at the interface of coating and counterpart. This is graphitization process that develops on the H-DLC surface. These results are also in agreement with [10,26] where the CoF of the H-DLC is attributed to the high coating hardness. It was also demonstrated by Costa et al. [4] that the CoF of the DLC in 3% NaCl after 1000 cycles reached 0.11.

The graphitization of the wear track was confirmed by Raman spectroscopy (Figure 2b). Raman spectroscopic measurements were performed at several locations of the wear track at the end of the sliding test of the H-DLC coating. The spectra have D and G peaks of 1362 cm^{-1} and 1573 cm^{-1}, respectively. The ratio of D and G peaks (I_D/I_G) is 0.82. Therefore, comparing the Raman spectroscopies (Figure 2 a and b), the ratio of D and G peaks I_D/I_G increased from 0.42 for the virgin coating to 0.82 after the wear test. According to Costa et al. [4], the increase of ID/IG ratio indicates the formation of a graphite layer over H-DLC surface during the tests. The phase of diamond-like (sp^3 – D band) transformed in graphite-like structures (sp^2 – G band) because of the stress-strain state imposed by the sliding friction of the tribo pair.

It should be noted that the above analyses were done only for H-DLC coating because Si-DLC coating exhibited significant spalling and delamination in all test conditions. Therefore, the coefficient of friction values with contact pressure of 150 and 400 MPa (see Table 1) are almost the same to Si-DLC coating. It probably occurred because with contact pressure of 150 MPa was already sufficient to cause damage on the coating surface.

The measurements of wear scars diameter on the silicon nitride balls and the wear rate are shown in Table 2. The largest diameter of wear scars, for each coating, correspond to the highest load under dry conditions. The wear scar diameters and wear rate for Si-DLC were consistently higher than H-DLC; this seems linked to the Si-DLC having a higher CoF compared to H-DLC under all conditions (Table 1). The mass loss of DLC surfaces occurred in all tested conditions, being less for the contact pressures of 150 MPa and wet conditions.

Table 2. Diameter of wear scars on the counterparts (Si_3N_4) and wear rate for different environments and contact pressures.

Contact Pressure (MPa)	Condition	Diameter (mm)		Wear Rate (mm^3/N.m)	
		Si-DLC	H-DLC	Si-DLC	H-DLC
150	Dry	0.987	0.429	1.30E-07	5.57E-09
	Wet	0.790	0.328	1.72E-07	4.60E-10
400	Dry	1.302	0.770	1.03E-06	5.83E-09
	Wet	1.197	0.665	3.29E-06	5.54E-09

A comparison between the wear rates of the coatings tested at different conditions and contact pressures is also shown in Table 2. Dry conditions (high friction) with higher contact pressures as expected was the most severe test. Si-DLC showed the widest wear tracks and highest wear rates due to an adhesive failure. This result could be likely attributed to the resistance to wear in terms of the hardness, ductility and stiffness of the coatings. As previously determined, the hardness and elastic modulus of Si-DLC coating were 30% and 26% respectively; noticeably inferior to H-DLC coating.

Table 2 shows that H-DLC presented consistently lower wear than Si-DLC. Results are proved by SEM micrographs and EDS (Figure 4). A better adhesive strength was observed on H-DLC, i.e. its surface did not undergo adhesive failure after wear test under dry and wet conditions at lower contact pressures (Figure 4 a and b). However, when increased the contact pressure occurred detachment of the coating (Figure 4 c and d). Si-DLC did not exhibited sufficient adhesion under both dry and wet conditions at lower contact pressure (150 MPa) (Figure 4e). The detachment occurred along the wear track after sliding.

Despite knowing that higher stresses in the contact promoted graphitisation of the H-DLC, particularly under dry conditions, it should be noted that the carbon transfer weakens the coating structure and above some critical point when coating cannot withstand higher loads and failures arose from the detachment of the coating by interfacial fractures with the consequent increase of wear (Figure 4c). Conversely, the H-DLC under wet conditions appears to be that graphitisation promoted by the impinged stresses in the contact is not completely suppressed since the carbon contents remain as graphically shown in Figure 4b and d. Analogously, it is also in agreement with behaviour of the CoF, where the variations of the CoF are scarce (Figure 6). For Si-DLC coating, the lacking of adherence of the coating was observed in all test conditions. Analyses by EDS linescan shows enough evidence of the delamination failures, as can be seen in Figure 4e.

Figure 3 c-f shows AFM analysis of H-DLC worn coatings under dry and wet conditions at contact pressures of 150 and 400 MPa. In both conditions, an increase in the surface roughness was identified, although, as expected to a lesser extent for the lowest loads. Again, no measurable features are given for Si-DLC coating because of the delamination failures throughout the tests.

3.3 Electrochemical properties

Figure 7 shows anodic polarization curves obtained in naturally aerated 3.5% NaCl solution and Table 3 shows the polarization curves data. Tests were carried out on H-DLC and Si-DLC coatings before wear test and H-DLC film after wear test with 150 MPa of contact pressure and wet condition. This latter condition was selected because it was the only condition found without any substantial adhesive failure on the coating surface, as demonstrated by SEM/EDS examinations (see Figure 4 b).
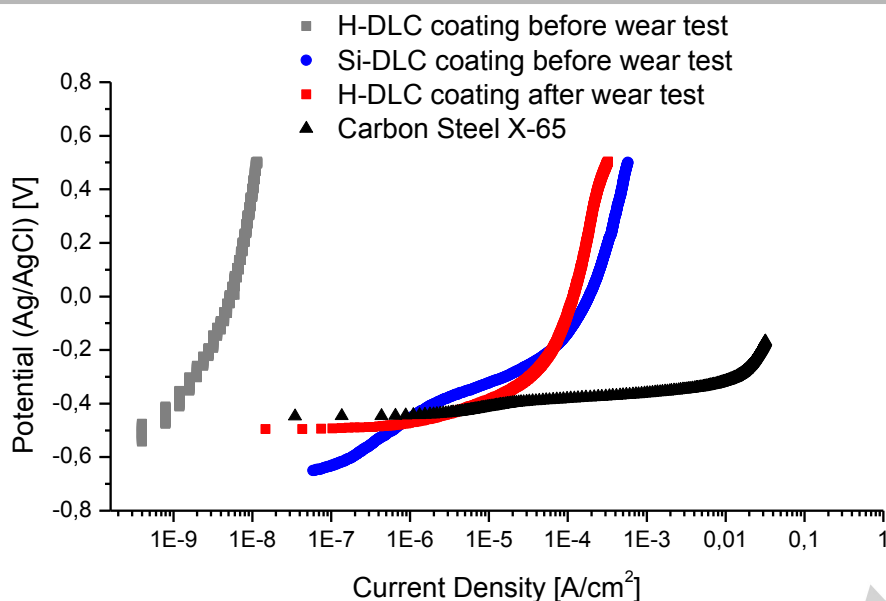
Figure 7. Anodic polarization curves of H-DLC and Si-DLC coatings and bare steel in 3,5 % NaCl, naturally aerated, pH 7

Table 3. Open circuit potential (OCP), current density values measured at 200 mV above the OCP.

Sample	OCP (V) (Ag/AgCl/KCl)	Pot. (V) 200mV above OCP	Log i (A/cm²) 200mV above OCP
Steel	-0.477	-0.247	2.21E-02
H-DLC – Before wear test	-0.543	-0.343	1.60E-09
H-DLC – After wear test	-0.496	-0.296	3.44E-05
Si-DLC – Before wear test	-0.676	-0.476	7.67E-07

H-DLC film (before wear test) had an initial OCP of -0.543 mV and after wear test of -0.496 mV, indicating that after wear test approximated to the OCP of carbon steel (-0.477 mV). It probably happened because of the presence of Nano-defects on the H-DLC surface provoked by wear test. Plus, the galvanic couple formed between the H-DLC coating and the surface of carbon steel is very low because of the narrow difference between these OCP values. These results are in agreement with the literature

[1,5] . Wang et al. [5], claim that if there is a failure on the surface of the DLC film exposing the metal surface, the localised corrosion could be easily inhibited by virtue of the DLC film and carbon steel have almost the same OCP. Consequently, the H-DLC provide a good improvement on the integrity against internal corrosion in carbon steel, given the protective barrier of the film and by obstructing the pitting corrosion process on the bulk carbon steel. These results are in accordance with Hadinata et al. [17], where the coated samples without defects and with defects had similar OCPs in relation to the OCP of the carbon steel. The Si-DLC revealed a more negative OCP (-0.676 mV) than the H-DLC. Thus, the galvanic couple between this Si-DLC film and carbon steel is larger.

The H-DLC and Si-DLC coatings prior the wear assessment, revealed an increased corrosion resistance compared to the carbon steel as expected. The carbon steel, in turn, exhibited active dissolution in the solution (Figure 7). The corrosion current density measured at 200 mV above OCP (Table 3 and figure 7) was 2 orders of magnitude higher on carbon steel than DLC coating. Before wear tests, H-DLC was around 10^{-9} A.cm^{-2} and after wear tests were around 10^{-7} A.cm^{-2}. For Si-DLC, corrosion current density was 10^{-5} A.cm^{-2}. Comparing these values with the corrosion current density of carbon steel (10^{-2} A.cm^{-2}), even with defects DLC films presented less anodic current density than carbon steel. This occurs probably because the exposed area of carbon steel due to nano defects of DLC after wear tests were much smaller than the area of carbon steel specimen. Therefore, these values are important to compare results of each condition, showing that anodic current density increased on DLC coatings with defects. However, to measurement the corrosion rate underneath the porous regions of the DLC film is difficult due to the need of measure the exposed area of the bulk into the DLC defects.

Galvanic couple formed between DLC films and carbon steel surface can be influenced by two factors: OCP and conductivity [1,5,27]. H-DLC film before wear test had an initial OCP of -0.543 mV and after wear test of -0.496 mV, which was close to the OCP of carbon steel (-0.477 mV). This behaviour could be a secondary effect related to nano-defects imposed on H-DLC by the wear test. Plus, galvanic couple formed is very low due to the slight difference between OCP values.

Si-DLC OCP was more negative than the H-DLC. Thus, galvanic couple between Si-DLC film and carbon steel is higher. These results are in agreement with the literature [1,5]. Wang et al.[5] claim that if there is a failure on the surface of the DLC film exposing the metal surface, the localized corrosion could be easily inhibited due to DLC film and carbon steel to have similar OCP. Hadinata et al. [17] reported that the coated samples with and without defects presented similar OCP to carbon steel. However, conductivity could decrease corrosion resistance of the DLC film and affect negatively galvanic couple DLC/Fe. According Miyagawa et al. [27], DLC coatings present high electrical resistivity, around 10^2 to 10^6 Ω cm. The wide range of values are associated with the deposition technique and conditions.

It has been reported [7–10,14–17] that the DLC has a lower anodic density current than the carbon steel, around nA/cm^2, but they do not correlate this DLC density current with dissolution processes of the DLC coating or bulk material. In fact, two factors need to analysed in this context. The first one is that this small current density could be associated to pores in the DLC film. Plus, according to Reisel et al. [8] the DLC is inert, amorphous and does not corrode, so this anodic current is not associated to the passivation process; and the amorphous structure of the DLC coating reduces or halts the electron transport over the DLC surface. Therefore, this low anodic density current is probably associated to two facts, being nano-pores on the DLC films and the ion flow.

Films with nano-pore defects can easily be penetrate by the solution. By this mechanism, the solution could reach the carbon steel surface (inner layer) and trigger the corrosion process on the bulk material. However, films free of nano defects effectively protect the carbon steel inner layer from fluid ingress. The ionic transportation process on the substrate (under DLC surface) is related to water dissolution as the following reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
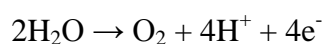
The Si-DLC begun with a low anodic current but it increased after applying some anodic potential (Figure 7). This is likely to be because some defects and the anodic polarization on the surface. The process of film deposition could create some nano scale defects and then, during the anodic polarization, high imposed anodic potentials could promote the diffusion of ions inside these defects, commencing the corrosion process on

the metal surface [5]. From the mentioned, it is need to study if nano defects on the film could resist to ionic diffusion forces during long periods of exposition to a corrosive environment.

The lowest anodic current of the H-DLC coating (before wear testing) suggests that this film has excellent resistivity to be used as a corrosion barrier in oil and gas equipment made of carbon steel, which is a good property against corrosion process in saline solution (see Table 3). In addition, it proves that the film was deposited without a significant defect on the carbon steel, as indicated in Figure 2, where it is clear the excellent adhesion of the coating to the substrate and exhibiting a structure without adhesive failures, i.e. with an interface of high quality with respect to the carbon steel.

The only wear test that did not show evidence of coating damage was that of 150 MPa contact pressure and in wet conditions. However, the anodic current of the H-DLC (post wear test) increased in relation to the H-DLC (before wear test), indicating that the wear test produced some nano defects on the H-DLC film surface. Nonetheless, these Nano defects were not observed by SEM/EDS (Figure 1). Therefore, this ramp up on the anodic density current could be associated with the process of substrate anodic dissolution. It means that 150 MPa was sufficient contact load to produce nano defects on the H-DLC surface and to expose the substrate to the corrosive solution.

Figure 8 shows the H-DLC film surface after the wear test in wet condition and with contact pressure of 400 MPa. From the SEM secondary electron image, it was noticed a hole of around 200 μm, in the multi-layered H-DLC film. The hole exposed the carbon metal causing the corrosion process. It may be inferred that this delamination of the H-DLC film occurred during the wear test. However, the good information is that the corrosion process occurred only at the location where wear test promoted the defects and it did not propagate between the interface of H-DLC film and substrate. Even with some defects, the H-DLC is a good option to reduce the corrosion rate of the carbon steel to prolong the service life of the equipment utilised in oil industry. According to Sharma, Barhai and Kumari [15], the DLC coatings are chemically inert, at room temperature, for almost all acid, alkalis and organic solutions and solvents. Because of its good corrosion resistance and excellent adherence to the carbon steel substrate, the H-DLC has a strong potential to be used for important parts and equipment of the oil and gas industries for instance, the SSCV, pistons and pumps, associated to pipelines.
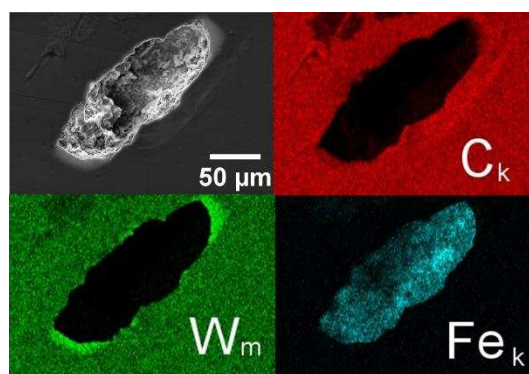
Figure 8. H-DLC – SEM secondary image and EDS mapping of the defect caused by wear test (400 MPa and wet condition).

In medical applications like ankles, wear-corrosion solicitations caused failure on the DLC film [3], demonstrating that the DLC film did not have good results with regard to wear and corrosion processes acting together for this environment. Conversely, the results in this work elucidated that the resistance of the H-DLC film, applied over carbon steel, had better performance than Si-DLC in situations where the equipment are subject to conditions of wear and corrosion acting together in saline environments.

DLC films have poor adhesion on carbon steel that contributes to the spontaneous debonding effects. A variety of metallic and intermetallic interlayers (Al, Cr, W, Ti, Si) are used to improve the adhesion properties, corrosion resistance and reduce the number of critical film defects of DLC on carbon steel. This prevents premature delamination under both higher loads and contact pressure during tribocorrosion conditions [28–30]. Reisel et al. [8] showed that the electron transport through the diamond-like carbon coating is reduced or even stopped by the amorphous structure of the layer. The fraction of metallic layers could lead to increase electron conductivity. Multi layers and single layers coatings presented different behaviour in relation to electrochemical behaviour, being better for multi layers coatings than single layers. In the present work, the interlayer of Cr/W could improve the electrical conductivity on the defects. However, further investigation is need, once it was not possible to evaluate the influence of Cr/W interlayer in wear and electrochemical tests for both films had the same interlayer.

Figure 9 shows the EIS curves obtained at the open circuit potentials of the steel, H-DLC and Si-DLC coatings before wear test and H-DLC film after wear tests with 150 MPa of contact pressure and wet condition.
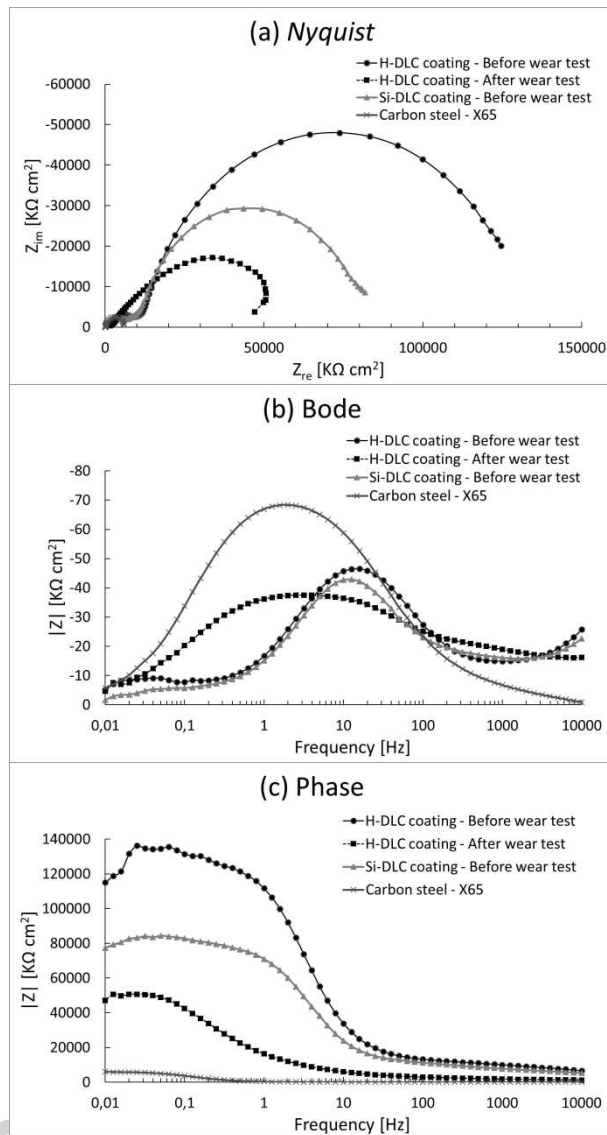

Figure 9. EIS behaviours for carbon steel, HDLC and Si-DLC films. (a) Nyquist plots, (b) Bode plots and (c) Phase plots.

The Nyquist plot (Figure 9a) shows different behaviours of carbon steel, H-DLC and Si-DLC coatings at locations of high frequencies, with values of imaginary and real components of $M\Omega cm^2$ for both DLC coatings and $K\Omega m^2$ for the carbon steel. The same performance is observed in intermediary and small frequencies, where both DLC coatings presented higher values of Z_{real} and Z_{imag}. These results suggest that both DLC films have a higher capacitance than carbon steel. It occurred due to the carbon steel had

activated dissolution without presenting any passivation process, as showed in the polarization curves (Figure 7). Therefore, the capacitive arc of both DLC coatings is so much higher that the carbon steel, showing the good polarization resistance and high resistivity of the coatings. The Si-DLC presented a capacitive arc smaller than H-DLC. These results agree with the polarization curves (Figure 7) where the Si-DLC had more anodic density current than the H-DLC coating.

Impedance module Bode plots shows at high frequencies (1 KHz until 100 KHz) that the Z module is almost constant and phase angle ϕ are near to zero for the carbon steel. This characteristic represents the resistive behaviour of the solution. However, the phase angle of both DLC films is higher, where the resistive behaviour of the solution is associated with the inert conditions of both DLC films.

It should be noted for low frequencies that both DLC films had higher Z module than the carbon steel (Figure 9c), showing the excellent corrosion resistance of the DLC films. Therefore, the electrochemical corrosion reactions followed between the interface of DLC films and metal substrate as it had a very small contact time. Thus, the ions transport related to the corrosion process at the metal substrate could hardly be avoid because of the layer of DLC film [5]. The reduction of Z module of the H-DLC before wearing test to H-DLC after wearing test and Si-DLC coating can be associated to Nano defects on the films surfaces.

Bode plots (Figure 9b) shows that the impedance process moves from Ohmic to capacitance dominance. The phase shift moves from 0 to -68^0 to carbon steel, 0 to - 38^0 to the H-DLC film before wearing test, 0 to -42^0 to the H-DLC after wearing test and 0 to -45^0 to the Si-DLC coating. Plus, it also shows that there is one constant time or maximum angle for the carbon steel, while there are two constant times or two maximum angles for both DLC coatings. This angle at high frequencies could be associated to the inert property of the DLC films, acting as a barrier to the process of charge transfers (electrochemical reactions) at the interface of DLC films and electrolyte. The angle in intermediary frequencies could be associated to the capacitance of the DLC films (CPE_1).

The equivalent circuits (Figure 10) of the EIS were used to assess the mechanisms of corrosion process that ensued at the interface of electrolyte/carbon steel and electrolyte/DLC coating systems. The equivalent circuit of both DLC coating has been used [5,7,14] to explain the AC response of the DLC coating on a metallic bulk

material. Thus, the DLC equivalent circuit is composed by: Tested electrolyte resistance (R_e); capacitance of the DLC coating, being a constant phase element (CPE_1); resistance to charges transference at the interface of DLC film and electrolyte, external layer of the DLC film associated to some areas of the surface film that has ionic conduction, named porous resistance (R_1); the elements R_2 and CPE_2 represent the polarization resistance of charge transfer and capacitance of interface of the DLC film and metal substrate, which means that is the internal layer of the DLC film. The carbon steel equivalent circuit is composed by: Tested electrolyte resistance (R_e); capacitance of the carbon steel, being a constant phase element (CPE_1) and resistance to charges transference between the carbon steel and solution (R_1).
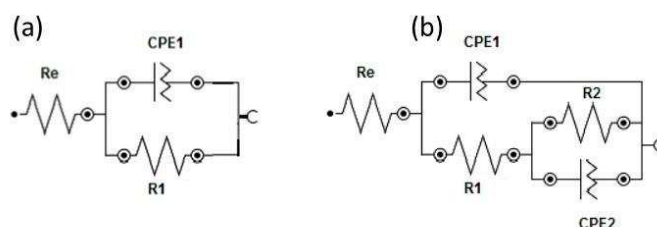

Figure 10. Equivalent circuit of (a) carbon steel and (b) DLC films coatings.

In high frequencies, the impedance of the DLC films has a dominating Ohmic behaviour, being controlled by Ohmic of the electrolyte resistance (R_e). In intermediary frequencies, the system is controlled by the capacitance of the DLC coatings (CPE_1) and the resistance to charges transference at the interface of DLC films and electrolyte (R_1). Moreover, in low frequencies (10^{-3} to 10^{-1} Hz), the impedance is managed mainly by the polarization resistance of charges transfer between the interface of the DLC films and metal substrate (R_2) and by capacitance of interface of the DLC films and metal substrate (CPE_2). This results are in accordance with Liu and Kwek [14].

4 – Conclusion

The purpose of this research was to evaluate tribocorrosion behaviour of hydrogenated and silicon DLC coatings on carbon steel. The approach used to investigate the problem was sliding wear test on pin on plate machine, plus electrochemical and electrochemical impedance experiments. As a result of this work, the following main findings concerning the nature of wear were:

1) Tribology tests showed poor performance of Si-DLC coating, which presented total delamination in all contact pressure applied. H-DLC exhibited high incidence of coating damage under the conditions tested, except when applied a contact pressure of 150 MPA in wet condition. Although there is an absence of visible defects on H-DLC coatings under these conditions, electrochemical tests showed an increase of corrosion. It means that 150 MPa was enough pressure to produce nano defects on the H-DLC surface, exposing carbon steel substrate to the corrosive solution.

2) The lowest anodic current of the H-DLC coating suggests that this film has excellent resistivity to use as a corrosion barrier in oil and gas equipment made of carbon steel. It was proved to have an excellent adhesion of the coating to the substrate and to be effective against the corrosion process in saline solution.

5 – Acknowledgement

6 – References

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Highlights

- H-DLC showed an excellent adhesion to the substrate.
- The H-DLC coating had superior wear performance than Si-DLC.
- Tribology tests showed Si-DLC coating total delamination in all contact pressure applied.
- H-DLC was effective against the corrosion process in saline solution.