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Mechanical and corrosion behavior of thick and soft DLC coatings

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ABSTRACT

The DLC coatings are chemically inert, have low friction coefficient and good wear resistance. Depending on H content and sp³ bonds, they can be classified in “soft” or “hard” films. In this work, the corrosion and mechanical behavior, as well as the adhesion of thick DLC coatings are studied. The coatings, which are in fact silicon containing amorphous hydrogenated carbon films, were deposited by PACVD on nitrided austenitic stainless steel (duplex sample) and non-nitrided austenitic stainless steel (coated sample). The films were characterized by EDS and Raman spectroscopy, hardness was assessed by nanoindentation and microstructure was analysed by OM and SEM. To evaluate sliding wear behavior and friction, pin on disk tests were performed. The abrasive wear resistance was tested using the ASTM G65–95 Dry Sand/Rubber Wheel test. Erosion tests were conducted in water and sand flux. The corrosion resistance was evaluated by the Salt Spray Fog Test and electrochemical tests. The adhesion was tested using Scratch Test. The purpose was to systematically characterize the defects present in these thick DLC coatings relating them to adhesion, wear and corrosion resistance.

The thickness of the DLC coating was about 37 μm, and its hardness was 12 GPa. The coatings presented a low friction coefficient, about 0.09. In the abrasive tests, the mass loss was negligible and in erosion experiments, the mass loss was reduced to 30%. Regarding the corrosion performance, the behavior in the Salt Spray Fog Test was good only in the duplex samples. In potentiostatic tests in 3.5% NaCl using steps, the current density increased at higher potentials for the duplex sample. Concerning the film adhesion, the critical load was also higher in these samples than in the coated ones. The nitrided layer was a good interface for reducing the stresses and improving the adhesion, which is relevant for the decrease of the propagation rate of corrosion, when traversing defects are formed in the coating.

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1. Introduction

Diamond-like carbon (DLC) is a generic term used to name a range of amorphous carbon films which includes amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) [1,2]. Hydrogenated amorphous carbon (a-C:H) films can be classified in soft or hard depending on sp³ bonds, hydrogen content and consequently its hardness [1]. These coatings can be deposited by different methods such as PAPVD (Plasma Assisted Physical Vapor Deposition) or PACVD (Plasma Assisted Chemical Vapor Deposition) [1]. The DLC coatings are characterized by low friction coefficient, chemical inertness and wear resistance [1,3]. The combination of these unique properties of the DLC films has attracted great interest in different industries including oil and gas, automotive, aerospace, medical, military and paper. In applications such as oil and gas production which include pipes, tubes and valves, there are

different degradation mechanisms including wear and wear-corrosion, and for that reason, thick and robust coatings are required, with high wear and corrosion resistance [2].

There are several works about hard and thin DLC coatings but it is not the case of high thickness DLC (above 10 μm) due the high internal stresses which develop during the film growing [4]. Different elements, such as Ti, Cr, Co, Ni, Al and Si, can be added to the DLC coatings (doped or alloyed DLC) to reduce the internal stresses and modify properties such as the surface energy, thermal stability and electrical resistivity [2,5]. The alloyed DLC coatings can be produced by PECVD process in which is possible to introduce different precursor gases during the treatment [6].

On the other hand, DLC coatings have adhesion problems when they are deposited on metallic substrates because the carbon diffuses into the steel and the coating growth is delayed [7]. In addition, the thermal expansion coefficients of coatings and steels are not compatible, generating poor adhesion and high internal stresses. Some interlayers or surface modification treatments have been developed in order to solve these problems [7–9]. Plasma nitriding processes can be a good pre-treatment option for the DLC coating deposition. Plasma or ion nitriding

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is a surface modification treatment which allows improving surface hardness by means of nitrogen diffusion. Plasma nitriding increases the fatigue strength and improves the wear resistance [10,11]. In austenitic stainless steels, a nitrogen expanded austenite phase, called S phase, is formed in the surface region after low temperature ion nitriding [11,12]. There are several publications about duplex treatments, combination of plasma nitriding and hard and thin DLC coatings deposition [9,13–15] however, there are not many contributions that include thick DLC coatings [4,16].

DLC coatings develop certain defects as they grow, which can be observed from above, and could influence not only adhesion but corrosion resistance as it was already reported [9,17–22]. In thick DLC films produced by DC pulsed plasma the occurrence and size of defects tends to increase, but they were not studied thoroughly up to now.

In this work, corrosion and mechanical behavior of amorphous hydrogenated carbon coatings deposited on nitrided and non-nitrided austenitic stainless steel are investigated. A detailed study of the defects including cross sectional analysis was performed, to determine their size and morphology, if they are passing through or not, and finally, their influence in wear and corrosion behavior is discussed.

2. Experimental

AISI 316L austenitic stainless steel was used as base material. Disk samples were machined from a steel bar, 25 mm in diameter, 6 mm in height.

Plasma nitriding treatments were carried out in an industrial reactor by means of a pulsed DC discharge, for 14 h at 400 °C, with a gas mixture 20% N₂ and 80% H₂, the bias voltage was 320 V and pressure was set in 2 mbar. The DLC films were deposited by the PACVD in the same reactor used for nitriding with hexamethyldisiloxane (HMDSO) and acetylene as precursor gases (8% HMDSO and 92% acetylene), at 425 °C and a pressure of 2 mbar, using 330 V bias voltage [4].

The coatings were deposited on nitrided and non-nitrided austenitic stainless steel, duplex and coated samples respectively. Also nitrided austenitic 316L stainless steel without any coating (referred as nitrided samples), and without any treatment, only steel (referred as untreated samples), were used a reference groups to compare results.

The films were characterized by energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. The nitrided layers and the coatings were observed by scanning electron microscopy (SEM) and optical microscopy (OM). The microstructure was analysed by X-ray diffraction (XRD). XRD measurements were performed with Cu-K α radiation in the Bragg-Brentano configuration. The hardness (H) and Young's Modulus (E) of the film were measured using a Hysitron TI900 Triboindenter with 9 mN load. The hardness of the nitrided samples was assessed with a Vickers micro-hardness tester, Shimadzu HV2 using 0.49 N load.

The tribological behavior was evaluated by rotational sliding wear tests. These tests were carried out in a pin-on-disk tribometer using an Al₂O₃ ball (6 mm in diameter) as counterpart with a normal load of 5 N, resulting in a maximum Hertzian contact pressure of 0.78 GPa. The track radius was set in 7 mm, the tangential velocity in 10 cm/s and the total wear length was 500 m. The abrasive wear resistance was investigated using the Dry Sand/Rubber Wheel test according to ASTM G65–95 standard with an applied load of 45 N and a duration of 12 min. Prior to and after the tests, the samples were weighed using an analytical balance with a resolution of 0.1 mg. The mass loss was calculated to evaluate the abrasion resistance. The wear tracks were analysed with a 3D Zygo® Optical Surface Profiler which uses White Light Interferometry (WLI).

Moreover, erosion resistance was tested in a mixture of water and sand (AFS GFN of 50) flux with impact angle of 30°, during 1 h at a velocity of 7 m/s. Before and after the tests the samples were weighed with the above mentioned analytical balance. The eroded surfaces were examined by means of SEM. The film adhesion was characterized using the scratch test with variable load, starting with 1 N and load

increasing rate of 5 N/mm. A diamond tip of 200 μ m radius was used and a total distance of 10 mm was tested. The critical load was defined as the load at which the complete delamination of the coating was observed.

The corrosion behavior was evaluated by the Salt Spray Fog Test according to the ASTM B117 standard (atmospheric corrosion). Besides, potentiostatic tests using steps were performed in 3.5% NaCl solution. Three duplicates were made in each sample. The potential steps were of 200 mV and a duration of 1800 s each. The surfaces were observed with MO after the tests.

3. Results and discussion

3.1. Microstructure and mechanical properties

The Raman spectra were similar in both group of samples, nitrided and non-nitrided. D and G bands were identified as it can be observed in Fig. 1. The intensity ratio (I_D/I_G) was 0.95. Taken this value into account as well as the position of the peak corresponding to the G band and the three-stage model proposed by Ferrari et al. [14], it could be determined that this coating has a low proportion of sp³ C—C bonds of about 10%. Moreover, taken into consideration that the photoluminescence background of Raman spectra under the D and G peak spectral region increase with the increase of the hydrogen content, the ratio between the slope of the linear fitted background and the intensity of the G peak can be used to estimate the bonded H content [23]. In this case it was about of 43%.

In the EDS spectrum (not showed), Si and C were detected as it was expected. According to the previously mentioned results it can be concluded that these coatings are silicon containing amorphous hydrogenated carbon, which are identified by the acronym a-C:H:Si.

The coating thickness was about 37 μ m in both group of samples, with a well-defined interface with the substrate (Fig. 2). Some defects and inhomogeneities can be observed in cross section (SEM image), probably they were formed during the preparation process, grinding and polishing.

The total thickness of the nitrided layer was about 10 μ m with a double-layer structure. The outer layer corresponds to nitrogen expanded austenite and the inner layer corresponds to carbon expanded austenite. The carbon is a contaminant of the process due to the fact that the nitriding treatment and the DLC coating deposition were carried out in the same chamber [10,24].

The layer was not etched after the Marble attack as it can be seen in the optical micrograph (Fig. 3). No dark regions are observed, which

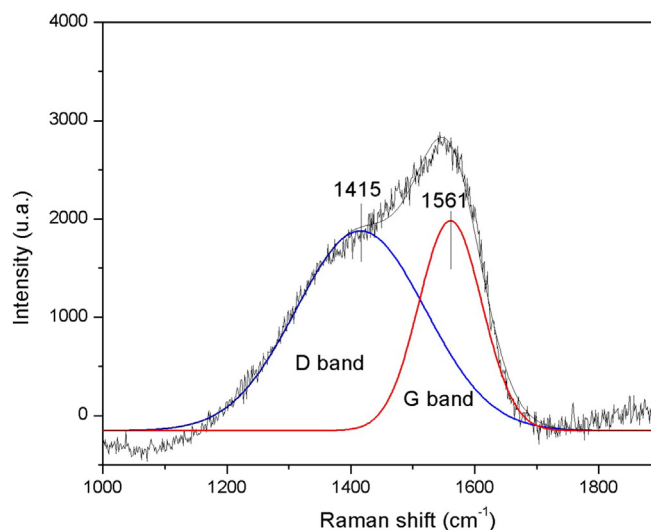


Fig. 1. Raman spectrum of DLC coating.

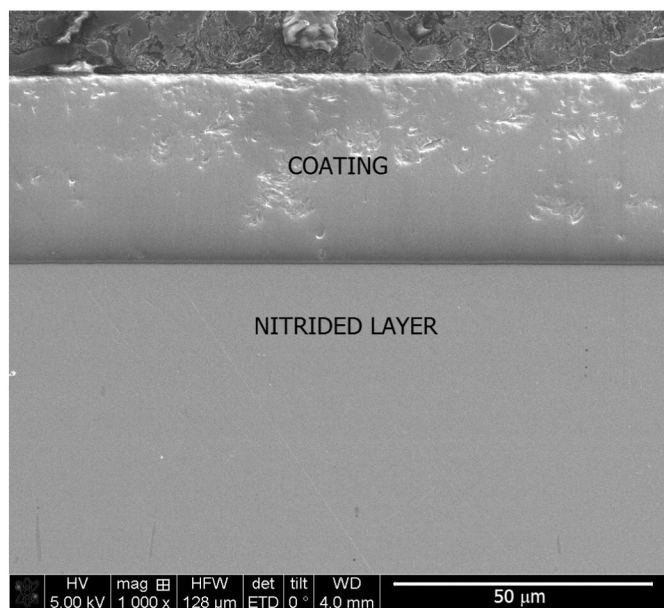


Fig. 2. SEM image of DLC coating in the duplex sample.

indicates a good general corrosion resistance and also that massive chromium nitrides precipitation did not occur.

The microstructure was analysed by X-ray diffraction in the coated samples. Fig. 4 shows the austenite and the expanded austenite peaks corresponding to the austenitic steel substrate, which were detected through the coating because this kind of DLC is amorphous, has a very low density and X rays are almost not attenuated until 50 μm . The peaks corresponding to the so call S phase are broader and shifted to lower angles respect to the original austenite peaks, indicating that the fcc lattice not only is expanded but also stressed, as it was reported in the literature for this nitrogen expanded austenite phase. Chromium and iron nitrides were not detected as it was expected, because the nitriding process was performed at low temperature and with a low percentage of nitrogen in the gas mixture [10,11].

The DLC coating hardness was 12 ± 1 GPa (the penetration depth of the indentation did not exceed the 10% of the film thickness). The nitrided layer hardness was 1010 ± 70 HV_{0.025} which correspond to 9.90 GPa. The coating Young's Modulus was 74 ± 6 GPa. According to the hardness and Young's Modulus, these coatings can be classified as "soft" [5].

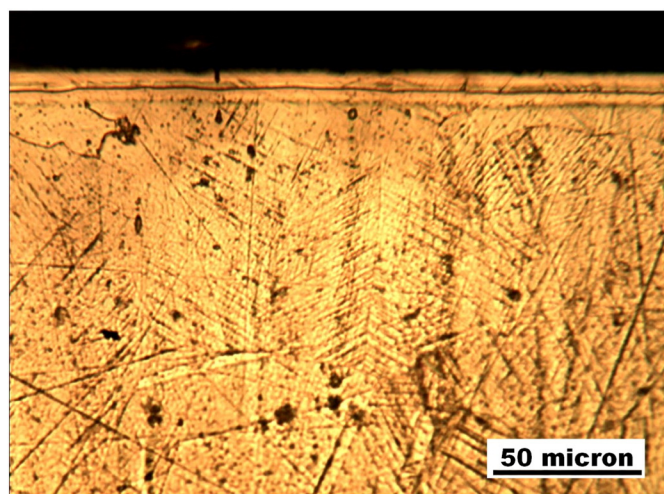


Fig. 3. Optical micrograph of nitrided layer.

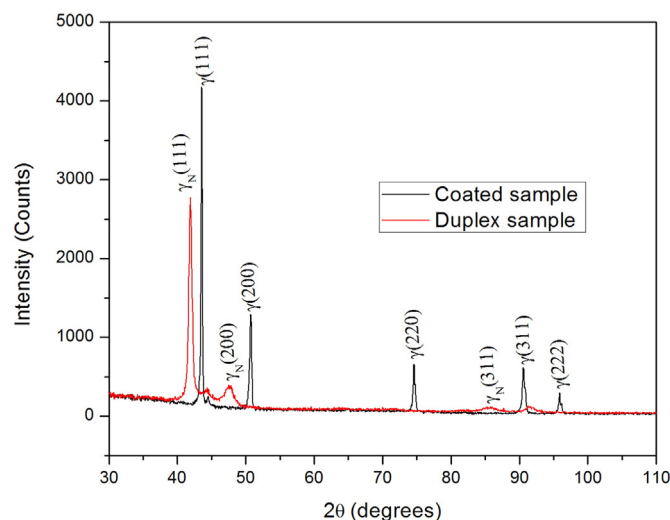


Fig. 4. Diffractograms of duplex and coated samples.

3.2. Surface morphology

Before the coating, the steel samples were mirror polished, and also before nitriding. But after the nitrided treatment, in spite of the fact that the samples were slightly repolished, the roughness increased from 0.040 μm to 0.070 μm . The surface morphology of the DLC was different in the coated from the one in the duplex samples. The defect size was different in the duplex sample than in the coated sample, and the density of defects was higher in the duplex sample than in the coated sample, probably due to the higher roughness and surface defects produced by the nitriding process previous to the DLC deposition (Fig. 5(a) and (b)).

In both type of samples the coatings presented defects of various shapes: protuberances or bubbles, bubble clusters, holes, some of them with sharp edge, as it can be observed in Fig 5(c) to (f).

The coating thickness is different in the region with hole-type defects. The presence of iron, chromium and manganese was identified in the EDS spectrum in the holes with sharp edge, signals coming from the substrate showing that the film thickness was substantially reduced (Fig. 5(h)). On the other side, the protuberances-like defects presented the same composition as the coating (Fig. 5(g)).

The formation of the defects depends on the surface condition, deposition rate, silicon content and position in the chamber [4,18]. In this case, the surface conditions were different (one group of samples was nitrided and another group not). Since in a DC plasma process the work piece is biased (or acts as the cathode), it is proposed that the charge is concentrated on the imperfections of the surface and the film grows differently, creating channels and defects in the shape of bubbles or protuberances on top. It is also possible that the holes with sharp edges were produced by a particle of dust which fell onto the sample during the coating process, and later was sputtered, leaving the hole behind.

The other hole-shaped defects could have the same origin, i.e. the protuberance was separated or detached from the rest of the coating, leaving the hole. This idea can be supported by a cross section examination of a bubble defect carried out with a SEM equipped with FIB (Fig. 6). It can be observed that beneath the bubble there is a crack, indicating that it could be detached due to internal stresses that develop as the film grows.

3.3. Wear behavior

In the pin on disk tests with Al₂O₃ counterpart, the friction coefficient was 0.09 for the only coated samples and 0.11 for the duplex

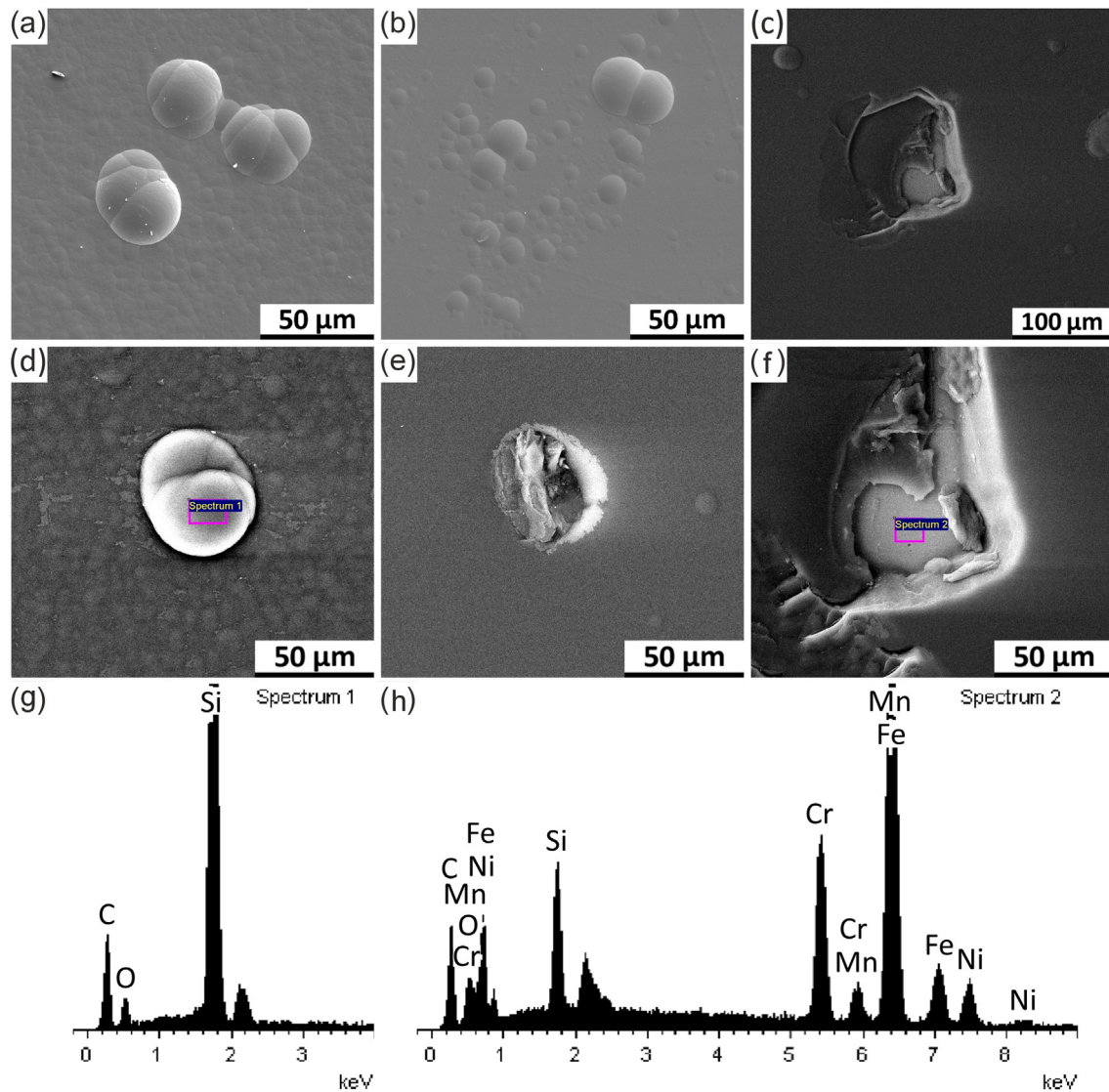


Fig. 5. Surface morphology of different samples (a) duplex sample, (b) coated sample, (c) to (f), surface defects, (g) to (h) EDS spectra of the defects. The figures (c) and (f) correspond to the same defect with different magnification.

ones. These values are in the range of those that have been reported for thin and hard films in the literature [3,25] and they are considerably lower than those for the nitrided samples without coating which have a friction coefficient of about 0.65 as it was reported in a previous

work [16]. The presence of DLC coating reduces the friction coefficient considerably.

According to the literature [1,3,5], the low friction coefficient of DLC films can be attributed to the presence of the graphite transfer layer

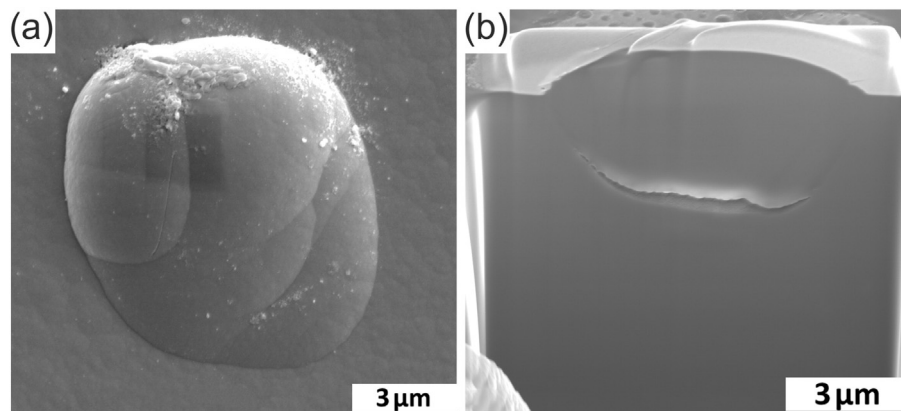


Fig. 6. (a) Bubble or protuberance defect, (b) cross section of the defect.

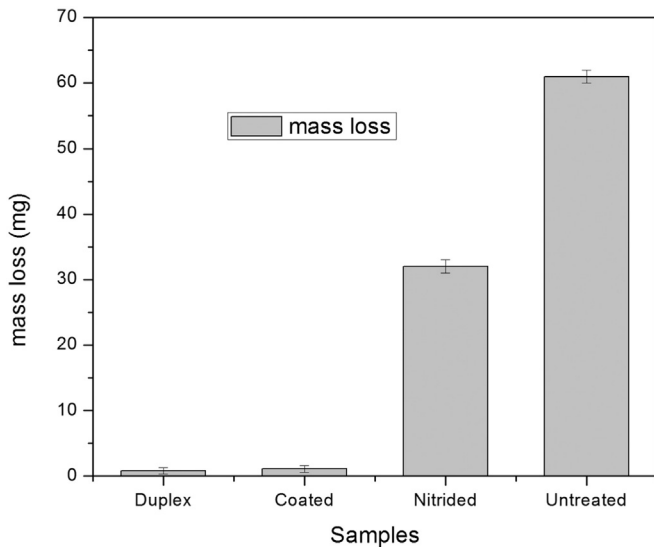


Fig. 7. Mass loss for coated, duplex, nitrided and untreated samples.

with low shear strength which is formed by the thermal and strain effects during the sliding. This layer has a self-lubricating effect [3,25]. Wear tracks in the duplex and coated samples were undetectable by a mechanical profilometer due to the elastic properties of the film, so it was not possible to calculate the lost volume in these tests.

After the abrasive wear tests, the mass loss was lower in the coated and duplex samples than in the bare materials as it can be observed in Fig. 7. In both group of samples, coated and duplex, the mass loss was similar and nearly undetectable because the mass loss fell within the

error. The damage was only superficial and it can be seen that the nitrided layer did not have any influence on the abrasive wear resistance.

The presence of the coating improves the wear resistance in comparison to the nitrided and untreated samples as it can be observed in Fig. 7.

In this type of severe wear tests, not only the hardness but also the strain tolerance and fracture toughness have influence on the wear resistance. The parameter H/E is the ratio of hardness (H) and Young's Modulus (E) and it is a way to characterize this synergy and normally in hydrogenated carbon films, H/E values are between 0.1 and 0.16, being higher than the H/E value for many metallic materials. This indicates that these coatings are strain tolerant [5]. Moreover, the H/E ratio is an indicator of film durability and it is related to failure capability [26]. From the results presented in 3.1, the H/E ratio was calculated and the value is 0.16 which is higher than that of the substrate (0.03), which explains their outstanding performance in this wear test.

In addition, these hydrogenated films have relaxation abilities (probably due to the free volume in their structures), i.e. they can recover part of their deformation as it was reported in the literature [5]. With respect to the morphology of the wear track, it could be observed that the DLC films showed small grooves along the track. Some damage was detected in a few regions where there were defects as it can be observed in SEM images (Fig. 8(a)). On the contrary, a far more severe damage was observed in the only nitrided (Fig. 8(b)) and in the untreated samples.

Furthermore, it could be observed that the defects on the surface (Fig. 5) disappeared after the abrasive wear tests and holes appeared in their place in both samples (coated and duplex). These holes did not pass through the coating thickness as it can be seen in WLI images (Fig. 9). It could be demonstrated that the presence of defects on the coatings did not affect the wear resistance according to the results reported above.

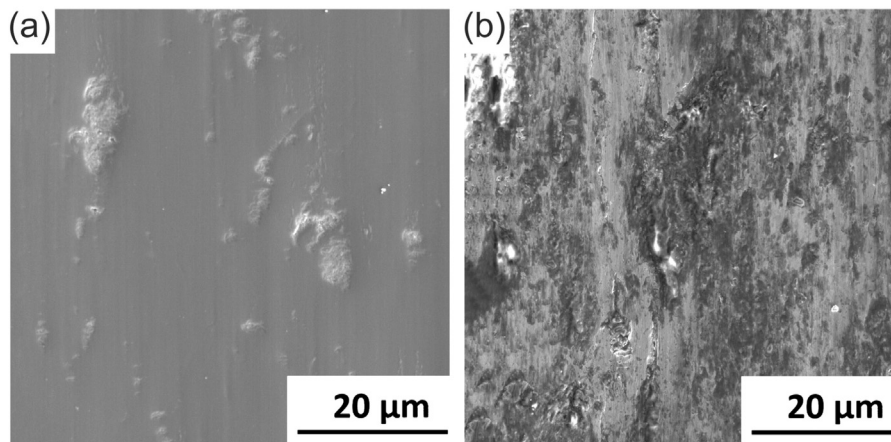


Fig. 8. SEM image of abrasive wear track of the samples (a) coated and (b) nitrided.

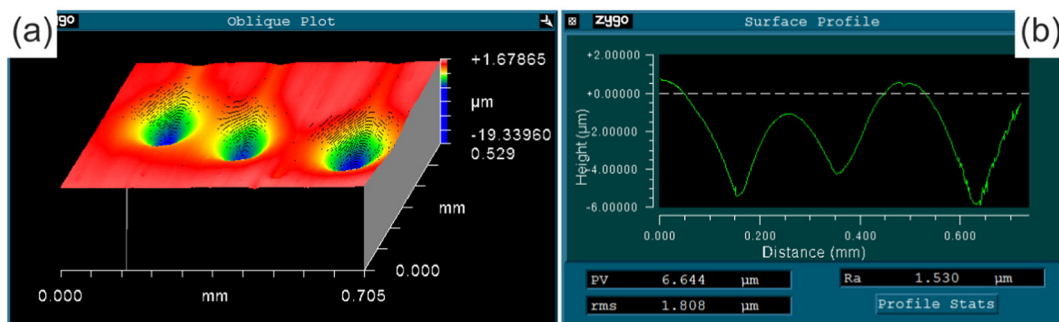


Fig. 9. White Light Interferometer image of abrasive wear track in duplex sample (a) 3D image, (b) profile which was obtained in the region with defects on the track.

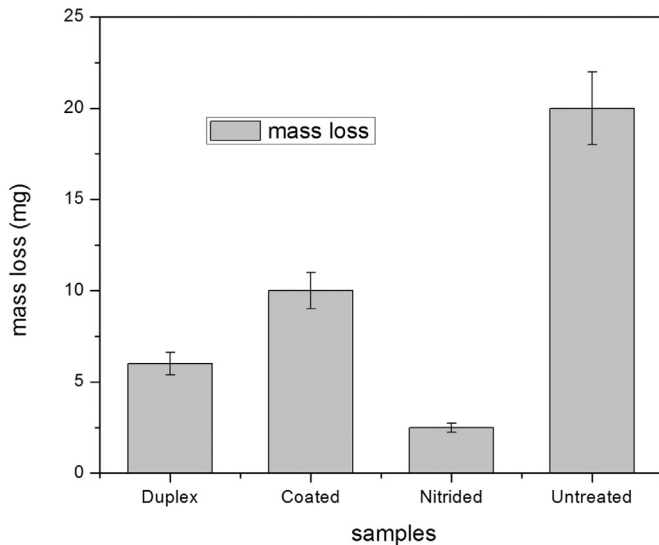


Fig. 10. Mass loss in the erosive wear tests for duplex, coated, nitrided and untreated samples.

In the erosive wear tests, the nitrided samples had a lower mass loss than the other samples (Fig. 10), due to the expanded austenite layer that increases the load bearing capacity and improves the wear resistance [14]. The mass loss of the duplex samples is attributed only to DLC film degradation and detachment. In this test, it was 6 mg, which are equivalent to 27% of its volume (assuming film density reported by Robertson for soft films [27]). As the nitrided layer beneath was not damaged, the DLC film can be considered a good protection.

Comparing the duplex and the coated samples, the mass loss was lower in the duplex, and this result is probably related to the adhesion. No regions with coating detachment are visible in the duplex samples surfaces (Fig. 11(a)). On the contrary, a region without coating can be seen in the coated samples with naked eye in the surface after the wear test (Fig. 11(b)). In this case, the mass loss is 10 mg, about 39% of the film volume.

The morphology of the eroded surfaces in the coated and duplex samples after 1 h of exposition is shown in Fig. 11(c) and (d). Small regions without coating could be detected in the duplex samples (Fig. 11(c)), and the coating detachment was extended in a whole region in the coated ones (Fig. 11(d)). The coating detachment indicates an adhesive failure of the coating in both samples.

Probably, the main cause for the removal of the coating from the substrate was not a progressive wear of the coatings but a development of a system of cracks generated by the impacts of erosive particles [28]. According to the literature, in this kind of test, the erosion process starts on surface cracks or in defects of the coatings. These cracks are propagated upon subsequent impacts of erosive particles and they can reach the substrate. If the coating is thick enough or most cracks are shallow, the cracks do not extend to the substrate [28,29].

When the coating adhesion is good, the coating surrounding the cracks remains intact and they do not extend to the substrate. On the contrary, when the coating adhesion is not adequate, the grooves reach the substrate and the coating fails, causing large pieces of the coating to flake off and the erosive wear process continues on the substrate [29].

In Fig 11(c) and (d) it can be observed that the film was detached and the substrate was exposed. As the adhesion was better in the duplex samples, the coating was detached only in some areas, indicating that not all the cracks and grooves could reach the substrate. On the

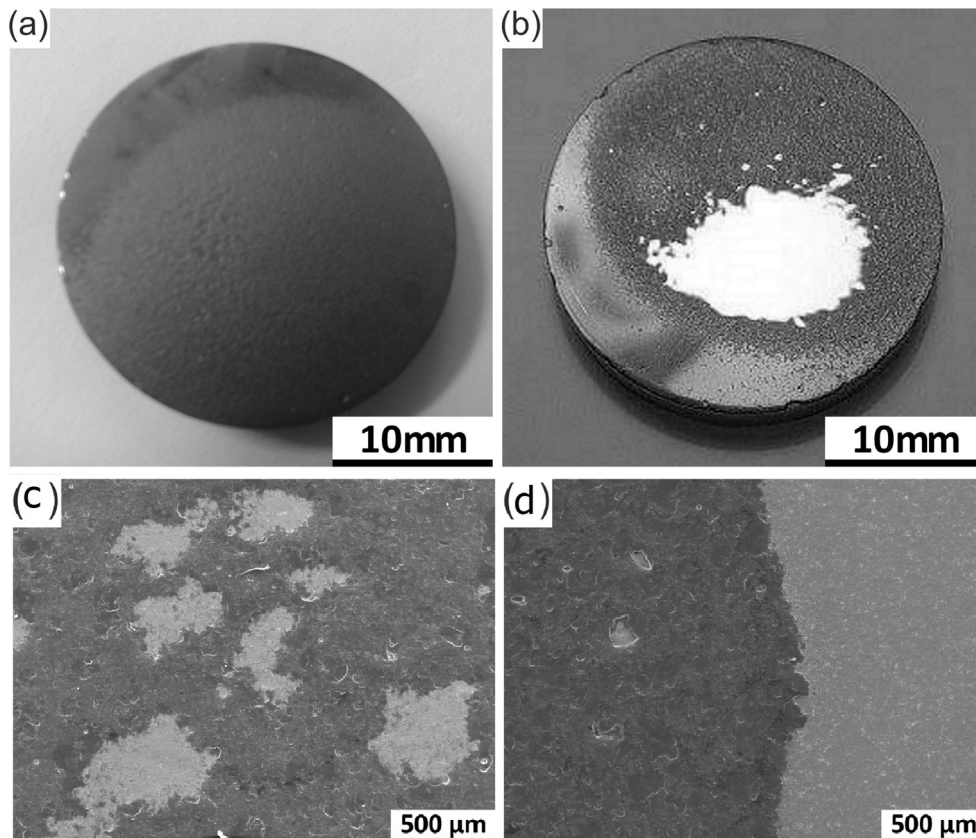


Fig. 11. Image of the surface of the samples after the erosive wear tests. (a) Duplex, (b) coated. SEM images of eroded region (c) duplex and (d) coated.

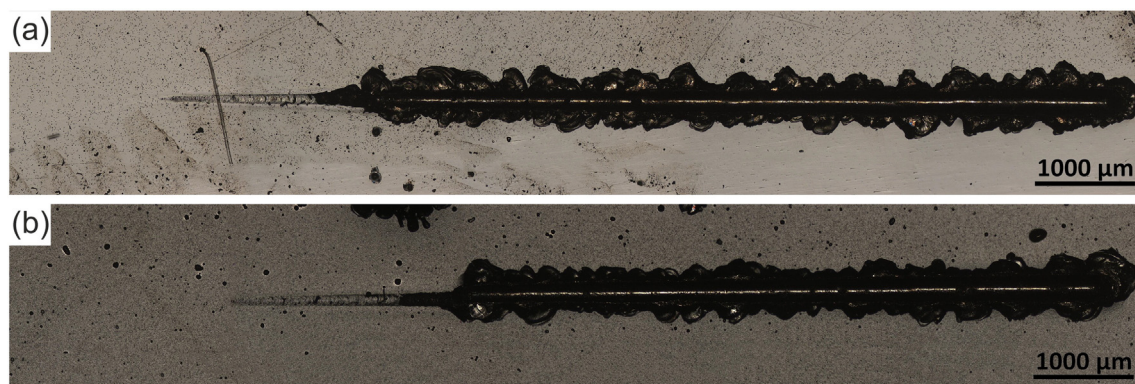


Fig. 12. Optical micrograph of scratch test tracks in (a) coated sample, (b) duplex sample.

other hand, in the coated samples the detached area was far more extended.

3.4. Adhesion

The adhesion was also better in the duplex than in the coated samples. The critical loads were (35.7 N) and (28.7 N) respectively as it is shown in Fig. 12. These critical load values are higher than those reported for titanium nitrides and oxides coatings [30,31], and even for some multilayers coatings [32]. This type of failure could be identified as wedging spallation, which is caused by the compressive stress ahead of the moving indenter and along the scratch groove. Compressive shear fracture of the coating and subsequent delamination is produced. The spalled areas tend to be semicircular and extend beyond the edges of the groove. This kind of the damage can be commonly seen in thicker coatings [27].

These coatings are thick enough to let the stresses be distributed more homogeneously in the coating, so they do not reach the interphase. Then, it can be proposed that these thick films delay the coating failure because they have a high load bearing capacity regardless of the substrate hardness [4]. This is the reason for the high values of the critical load measured in this test.

The duplex samples had the highest value because the nitrided layer improved the adhesion. This can be due to the positive effects of the increase of the substrate hardness, the reduction of the stresses between the coating and the substrate and the improvement of the load carrying capacity of the system, as reported by other authors [33].

3.5. Corrosion behavior

The salt fog spray test results indicated that the corrosion resistance was better in the duplex samples than in the coated ones, as it can be observed with plain eye on the surface after the test (Fig. 13). The coating was detached in a broad area of the surface in the coated sample as it can be observed in Fig. 13(b). It was confirmed by EDS analysis (not shown here) because signals coming from the substrate (Fe, Cr, Ni) were detected. Si and C signals were detected both in the center of the coated samples and in different regions of the duplex ones.

Although these coatings are known to be chemically inert and stable under most aqueous solutions, these coatings present defects which act as passageways that allow the contact of the corrosive medium with the substrate [4,34].

In these films, hole-shaped defects were detected, and as the adhesion in the coated samples turned out to be worse than in the duplex ones, it can be concluded that the interphase between the coating and substrate was weaker, producing the failure of the coating when the solution reached that part.

In the potentiostatic tests, once again the duplex specimens exhibited better corrosion resistance than the coated ones. An example is presented in Fig. 14. From the three experiments performed in different areas of each surface, in two of the three tests the current did not increase in the range of potentials used in these experiments, indicating that the DLC coatings are very insulating and act as corrosion barriers. In the other two curves there is an important increase in the current at high potentials. The breakdown potentials are not fixed, indicating that they depend on the magnitude of the diffusion path for the

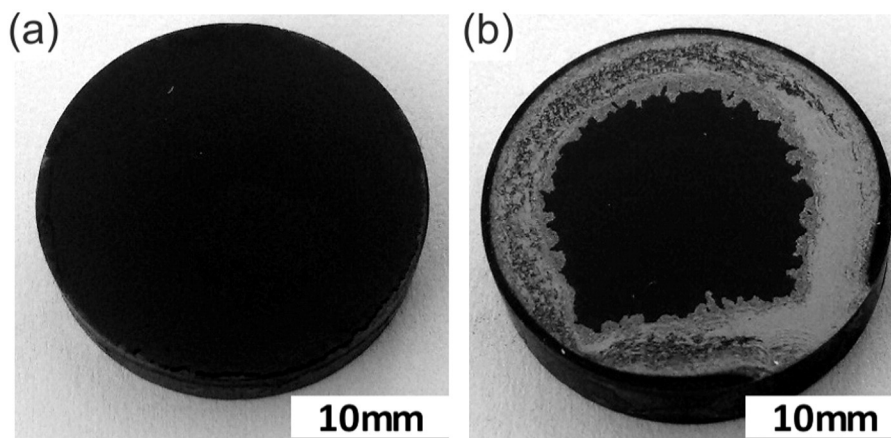


Fig. 13. Image of the surface of the samples after the spray fog test. (a) Duplex sample, (b) coated sample.

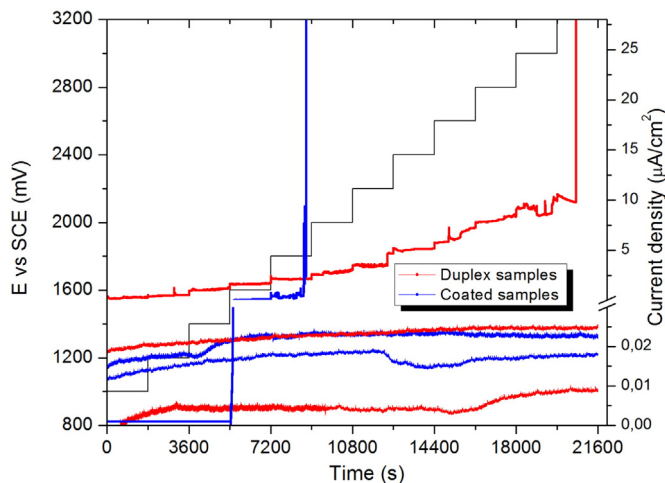


Fig. 14. Potential and current density in function of the duplex and coated samples.

electrolyte and on the increase of the affected area, which in turn depends on the dimensions of pre-existent defects in the coatings and also on coating adhesion. From all the duplicates a tendency could be observed. In a 70% of the tests the current remained in a very low value but for the rest it could be seen that the duplex specimens withstood higher potentials before breakdown, indicating that the better adhesion is determinant in the progression of the attack.

The corrosion behavior in this type of tests is related to the probability to find a surface defect in the tested area, and also to the size and type of the defects. As these coatings have good chemical inertness, they act as a physical barrier between the steel and the corrosion environment and as a consequence, the corrosion resistance at anodic potentials increases [35], but when defects are present, the thickness of the barrier changes and consequently the corrosion behavior is affected. Moreover, the defects can be passageways and act as channel connecting the solution to the substrate [4].

Taken into account the results presented above, it is proposed that corrosion initiation depends on whether the unavoidable microscopic defects can connect the corrosive media with the substrate, whereas propagation depends on adhesion. It is known that corrosion products can have a wedging effect and for that reason there are standard methods for evaluating adhesion degradation in corrosive environments using scribed specimens such as ASTM D 1654-08. Despite the fact that the defects mean size is higher in duplex than in coated samples, from the behavior found in the electrochemical potentiostatic studies, it can be concluded that adhesion has an important role and this is why the duplex specimens behave better when they are in contact with corrosive environments.

4. Conclusions

These thick DLC coatings presented low friction coefficient and good sliding wear resistance; these results are similar to those obtained in the case of hard and thin coatings. Moreover, the thick DLC coatings improved the wear behavior in abrasive situations regarding the untreated and nitrided samples. In the erosion tests, the mass loss was lower in the duplex than in the coated samples, and in the Scratch Test the critical load was higher in the duplex samples. Therefore, it could be assumed that even in thick films, the nitrided layer previous to the deposition of the coating improves the adhesion.

It could be observed that the corrosion resistance was also related to the adhesion, only the duplex samples presented good corrosion resistance. Finally in potentiostatic tests in a NaCl solution, the duplex samples needed higher values of applied potential than the only coated one, in order to show a breakdown behavior with a steep increase in the anodic current.

From the results it may be proposed that initiation of corrosion attack depends on the connection between microscopic defects and the substrate, whereas the propagation depends on adhesion.

The duplex system (DLC soft coating + nitrided layer) is a good option for applications where good sliding and abrasive wear behavior as well as corrosion resistance are required. The DLC film behavior in anodic polarization tests needs a deeper study, because a quantitative relation between defects and corrosion resistance should be found. It is also necessary to improve the adhesion resistance of the coatings to prevent the crack propagation, which can be the cause of failure in severe erosion situations.

Understanding the adhesion of protective coatings to substrates is critical for the prediction of coating performance.

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