

# Tribological behaviour of a multilayer CrN/DLC coating obtained using PVD-MS

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## Abstract

**Diamond-like Carbon (DLC)** coatings are used as protective layers for steel components due to their hardness, chemical inertia and interesting tribological properties. Reducing wear and friction coefficient is of great importance for industries today in order to increase energy efficiency and reduce harmful emissions to the environment. In this paper, a multilayer CrN/DLC coating is analysed. It was deposited using a commercial Plasma Enhanced Magnetron Sputtering over nitrided and not nitrided mild-alloy steel AISI 4140, produced for the first time in Argentina, at the firm Coating.Tech by Flubetech-Tantal. The base of the coating is an anchor layer made of CrN and the top layer is a chromium-doped hydrogenated amorphous carbon (a-C:H:Cr), which provides excellent tribological properties. Wear tests were carried out in a Pin-on-Disk apparatus, using an Al<sub>2</sub>O<sub>3</sub> ball as counterpart, with Hertzian contact stress from 1370 up to 1460 MPa. The friction coefficient was  $\mu \sim 0.1$ , which is 80% less than the untreated steel and the wear volume loss was **reduced eight times**. The adhesion was evaluated by means of Scratch Test, where major improvement was noticed in the samples which were nitrided as pre-treatment, increasing critical load from 25 N up to 65 N.

Keywords: DLC, carbon coating, tribology, PVD multilayer

## 1. Introduction

Surface engineering provides solutions through several techniques to improve the properties of surfaces, such as hardness, roughness, corrosion resistance, chemical affinity, hydrophobicity/hydrophilicity, texture, brightness, etc. The modification of the chemical composition of the near surface, for example nitriding of steels, or the deposition of coatings made of different materials are examples of these techniques, which are well known for the scientific community, but the industry is showing interest in their development and application in the last decade [1-3].

The use of hard coatings in Argentina up to these days is mostly limited to cutting tools made of HSS or cemented carbides, to protect and improve the duration of the cutting

edge. These coatings are usually made of titanium nitride (TiN) with its classic golden colour obtained by means of Physical Vapor Deposition (PVD) by a Cathodic Arc-Discharge [4-5]. In the agricultural and mining industry, thermal spray technology is used to deposit thick coatings for abrasion resistance [6-8]. Some coatings are also used with decorative purposes or as a protection against corrosion, e.g., electrolytic chrome plating, which today is forbidden in most countries around the world because of its hexavalent chromium cancerogenic effluent, that is bio-accumulative not only in the human organism but also on the ground, the water and from there to the whole ecosystem [9].

In recent years, the oil and gas industry, among others, is demanding solutions regarding the durability of machine components in harsh environments [10], thus increasing the

use of hard coatings and surface hardening processes to improve tribological properties and corrosion resistance. There are several kinds of coatings that can reduce the friction coefficient and the wear rate of materials, which will be useful to reduce operative costs, either fuel or electrical energy, but it will also reduce maintenance cost since its lower wear rate increases the life span of the components, thus fewer production stops will be needed to replace these elements. This means it is possible to improve the energetic efficiency, to increase profitability, and to reduce expenses.

Diamond-like Carbon (DLC) coatings are well known due to their high hardness, excellent tribological properties and good corrosion resistance [11]. A typical DLC coating is made of hydrogenated amorphous carbon or a-C:H. This amorphous phase is given by the mixture of carbon bondings as graphite-like  $sp^2$  and diamond-like  $sp^3$ , thus the coating is harder than the treated steel and shows a low friction coefficient which is attributed to the formation of graphite transfer layers. The addition of hydrogen causes a lower hardness, but it is useful to reduce the internal stress of the film. Besides, it has chemical inertia, thus it can be in contact with extremely aggressive and corrosive substances than would compromise the integrity of other different surfaces or films [12-13].

These coatings are usually grown using two main techniques: Chemical Vapor Deposition (CVD), where the material to be deposited is obtained through the chemical reaction of gas precursors, after which the compounds condensate over the substrate [14]. PVD on the other hand, uses a solid target of the desired material, from which the particles to be deposited are obtained by heat or sputtering, transported, and then adsorbed into the surface. Among several PVD techniques, the Plasma Enhanced Magnetron Sputtering (PEMS) consists in an ion bombardment of the target with an inert and/or a reactive gas to obtain the compounds, using a magnetic and electric field that help to concentrate the plasma in the target surroundings [15].

When these coatings are deposited over low or mild-alloy steels, which are relatively soft, the adhesion to the substrate can be compromised. To use these films over machine components, keeping a tough core but a hard surface with low friction coefficient, is necessary to implement a surface pre-treatment, e.g., ion nitriding, which is a plasma assisted thermochemical diffusion process [16]. This technique is well developed, and it has already been proved that the surface hardness gradient in the substrate helps remarkably to improve the adhesion of hard coatings over the above-mentioned steel substrates. The combination of two different kind of surface treatments in the same piece is known as a duplex treatment [17-18].

A collaboration project between the Argentinian companies Coating.Tech by Tantal Flubetech S.A.S., IONAR S.A., YPF-Tecnología S.A., and the Surface

Engineering Group (GIS) of the National University of Technology (UTN), Faculty of Concepción del Uruguay, allowed the realization of this paper, where a multi-layered DLC coating is characterized. This coating, sequentially produced inside the same PVD PEMS reactor, is developed for the first time in Argentina, which represents a great opportunity to enhance the national manufacturing with top-of-the-line technology. The influence of ion nitriding as pre-treatment is analysed regarding the adhesion of the coating and its wear resistance.

## 2. Materials and methods

In this work, mild-alloy steel samples of AISI 4140 were used. The chemical composition obtained with GDOES is in Table 1. The samples were cut from a normalized 25 mm round bar in flat discs with a thickness of 6 mm.

**Table 1.** Chemical composition of AISI 4140.

C%	Cr%	Ni%	Mo%	Mn%	Si%	S%	P%
0,42	0,98	0,15	0,19	0,85	0,27	<0,001	0,009

A thermal treatment was performed in order to obtain the highest toughness for this steel. Samples were austenised at 850 °C, quenched in oil and then tempered at 550 °C. According to the tempering diagrams, these parameters give the steel a high toughness, but also a low hardness. However, this high tempering temperature allows the samples to be heated in further treatments without altering the desired metallographic structure.

The surface of the samples was ground with SiC paper up to #1000 grit. They were analysed and tested in this “fine grinding” condition, to simulate the most commonly used roughness in the industry.

A group of samples were nitrided in an industrial plasma furnace, property of the company IONAR S.A. (Buenos Aires, Argentina). Ion nitriding was conducted at 500 °C for 25 h, using a gas mixture of 80% H<sub>2</sub> and 20% N<sub>2</sub> and a vacuum pressure of 5 mbar.

All nitrided and non-nitrided samples were coated with a multilayer film in a commercial reactor CemeCon CC800 DC Sputter (CemeCon AG, Germany), owned by the company Coating.Tech by Tantal Flubetech S.A.S. (Córdoba, Argentina). This equipment is a reactive PVD PEMS, where a chromium target with nitrogen as reactive gas is used to deposit the first layer, a Cr/CrN compound which acts as an anchor layer and mechanical support for the following layers. While the N<sub>2</sub> flow is fading out, acetylene flow is fading in, which creates in the surface a gradient of Cr compounds from nitrides, carbonitrides and finally carbides. The top layer, which is responsible for the tribological behaviour of the coating is deposited with a

hybrid process of PVD and CVD. The carbon for the DLC is obtained both from a graphite target using sputtering, and from an acetylene plasma discharge. A low activity on the Cr target during this last step provides the Cr-doping to obtain what is known as a-C:H:Cr (Chromium doped hydrogenated amorphous carbon) [19-21].

Surface hardness on heat-treated and nitrided samples were asset with a Vickers micro-hardness tester HMV-2 (Shimadzu, Japan) using a 50 g load ( $HV_{0.05}$ ). A nitrided sample was cut in half and hot mounted in phenol-formaldehyde resin to characterize the compound layer. Hardness gradient was measured in this cross section using the Vickers indenter with a 25 g load ( $HV_{0.025}$ ), in order to determine the penetration depth of nitrogen diffusion.

A SEM/FIB Helios Nanolab DualBeam (ThermoFisher, USA) was used to see the cross-section with the ion-milling tool and measuring the coating thickness. The elemental composition of each layer was obtained with EDS mapping.

To reveal the crystalline structure of the coating, grazing incidence X-Ray Diffraction was performed using a Cu anode in an XPERT equipment (Malvern Panalytical, UK). Since the carbon is not crystalline in the DLC coating structure but is an amorphous structure with C-C and C-H bonds, Raman spectra were acquired with a Raman inVia reflex system (Renishaw, Germany), scanning from 800 to 2000  $cm^{-1}$ , using a 50 mW diode laser which was kept below 50% of its full power. The bands D and G were identified, and the hydrogen content was estimated by the slope of the fluorescence background.

The mechanical properties of the film were determined with a Nano Indenter XP (MTS, USA) using a Berkovich tip and a 100 mN load, to ensure that the penetration depth is under the 10% of the coating thickness, avoiding any influence from the substrate.

Tribological properties of the coating were evaluated under sliding wear conditions using a home-made Pin-on-Disk tester, fabricated according to ASTM G99 standard. The disc is the sample, and the counterpart is a 6 mm  $Al_2O_3$  ceramic ball ( $E=343$  GPa,  $\nu=0.25$ ) [22]. The sliding distance was 1000 m, and normal loads of 10 and 12 N were used. Friction coefficient was measured in real time during the whole experiment. The wear track was measured with a mechanical profilometer SJ-210 (Mitutoyo, Japan) and was observed with optical and SEM microscopy, using EDS detector to determine any chemical change in the worn surfaces. All tests were carried out at room temperature which was  $(21.6 \pm 1.3)$  °C and the environmental relative humidity was between 44 % and 64 %.

The coating adhesion was determined using a variable load Scratch Tester Revetest Xpress+ (CSM Instruments, USA), applying a normal load from 1 to 101 N at a speed of 100 N/min, with a diamond Rockwell indenter of 200  $\mu m$  tip radius. Using an optical microscope, two critical loads were

determined:  $L_{C1}$ , where it is possible to appreciate the first cracks along the scar, and  $L_{C2}$ , the starting point from where the coating is fully delaminated. Rockwell C indentation was used to asset the fracture toughness of the coating. Even though this test is well known to evaluate the adhesion of the coating, according to VDI 3198 standard it is not reliable for films thicker than 3  $\mu m$ . However, it can give valuable information about the whole system behaviour when a high normal static load of 150 kg is applied during a 10 s timelapse [23-24].

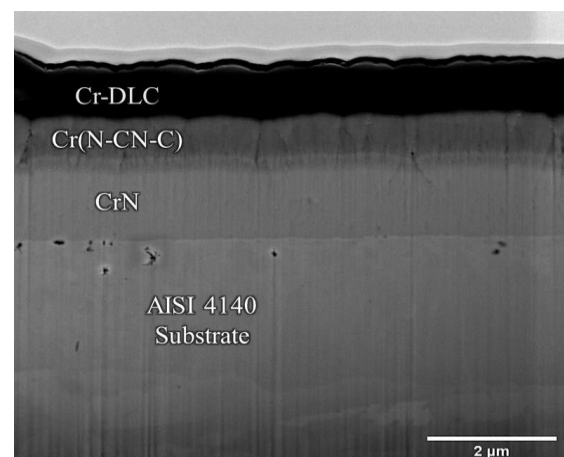
### 3. Results and Discussion

After heat treatment, core hardness of the tempered AISI 4140 steel was about  $(320 \pm 10)$  HV. Surface hardness after nitriding was about  $(650 \pm 25)$  HV. This is considered a low hardness value, which means the compound layer  $\gamma'$  is either very thin or is not present at all. This is the best surface condition for coating deposition, since the compound layer (often called the “white layer”), is hard but is also thin and brittle, which reduces its load bearing capacity. The hardness penetration profile showed a nitrided diffusion layer of about 300  $\mu m$  depth.

Base roughness of the samples after fine grinding with #1000 grit was  $(0.14 \pm 0.02)$   $\mu m$ . Nitrided samples were ground again with SiC paper #1000 grit for a brief time to have both conditions with the same roughness before the deposition of the coating.

#### 3.1 Coating Characterization

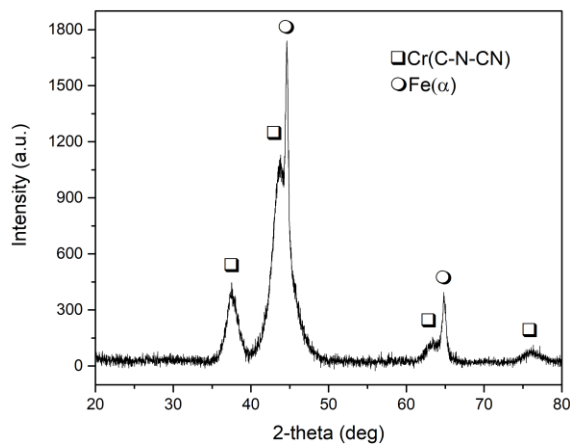
Using the SEM/FIB it was determined that the coating thickness was  $(4.0 \pm 0.1)$   $\mu m$ , with a DLC layer of  $(1.4 \pm 0.1)$   $\mu m$ , where the rest is the CrN and the Cr compounds gradient layers, which give the coating the load bearing capacity (Figure 1).



**Figure 1.** Cross-section of the coating obtained by means of SEM/FIB.

The chromium doping of the DLC determined using EDS was about 8% at. The mechanical properties were determined using a Berkovich nanoindentation. The Young Modulus was about  $(143 \pm 9)$  GPa and the Hardness was  $(12 \pm 1)$  GPa, which roughly translates to  $(1150 \pm 120)$  HV.

In the XRD spectrum of the Figure 2 it is possible to find the crystalline peaks of the iron of the substrate, as well as the chromium compounds from the anchor layer. Since both nitrogen and carbon have a small and similar atomic size, they both form interstitial compounds with the Cr atoms, which cannot be easily distinguished from each other. They could be defined as  $Cr_x(C,N)_y$  compounds.

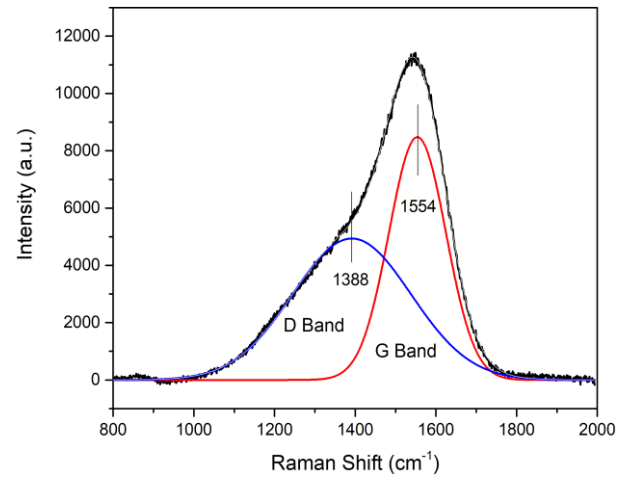


**Figure 2.** X-Ray Diffraction Spectrum.

The Raman spectrum in Figure 3 was fitted using Gaussian functions to show the typical peaks of a hydrogenated DLC, which are the graphite (G) and disorder (D) bands. The first was found at  $(1554 \pm 2)$   $cm^{-1}$  and represents the stretching vibration of  $sp^2$  bonds in form of both C=C chains and aromatic rings. The second peak, located at  $(1388 \pm 3)$   $cm^{-1}$ , represents the breathing mode of the  $sp^2$  graphite, but only for the aromatic ring structures.

Since the measured bands are shifted towards the centre if compared with typical values of  $1580$   $cm^{-1}$  for the G band and  $1350$   $cm^{-1}$  for the D band, and because of the D band (FWHM  $346 \pm 9$   $cm^{-1}$ ) is wider than the G band (FWHM  $165 \pm 7$   $cm^{-1}$ ), it means that there is a high disorder level in the amorphous structure. The ID/IG ratio is 0.58 with an error of 5.2%, this is the relation between the peak intensity of D and G bands.

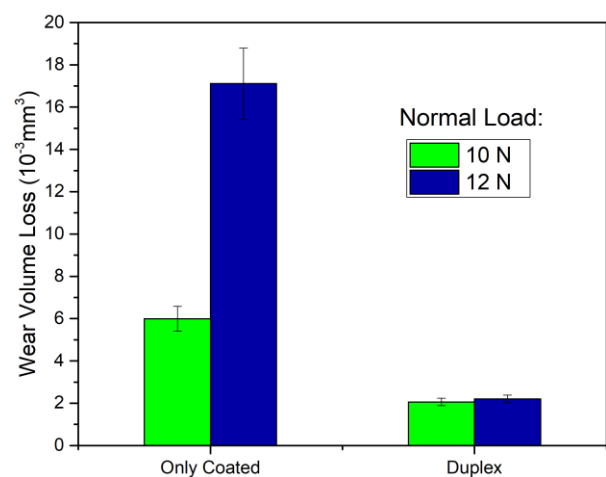
The hydrogen content was about 26%, which was estimated from the slope of the luminescence background in the visible Raman spectra, as proposed in the literature [25]. According to Robertson [26], when the coating has a hardness between 10 and 20 GPa and a hydrogen content between 30 and 40%, which is a close approximation to this particular case, it is classified as a hard a-C:H coating and the estimate content of diamond-like  $sp^3$  bonds is about 40%.



**Figure 3.** Deconvolution of the Raman Spectrum

### 3.2 Pin-on-Disk wear tests

In the wear tests using a 10 N normal load, the resulting Hertzian contact stress was 1373 MPa, considering a Poisson's ratio for a-C:H about  $\nu \sim 0.3$  [27]. The wear volume loss of the only coated samples was about  $(6.0 \pm 0.7) \times 10^{-3}$   $mm^3$ , while the duplex samples showed a wear volume loss of  $(2.1 \pm 0.1) \times 10^{-3}$   $mm^3$ , which is a difference of about three times between them, as can be seen in the bar graph in Figure 4. However, if they are compared with the nitrided samples (as many components are currently used in the industry), the wear volume loss was about  $(227 \pm 26) \times 10^{-3}$   $mm^3$  in the same conditions, which represents an increase of almost 40 times in the wear resistance if the DLC coating is used. This difference is even bigger when compared with the tempered material without any surface treatment, which had a wear volume loss of  $(760 \pm 85) \times 10^{-3}$   $mm^3$ .



**Figure 4.** Wear volume loss of the coated samples on the Pin-on-Disk tests.

For the higher normal load of 12 N, the Hertzian contact stress was about 1461 MPa. There is an even noticeable difference in the wear volume loss of both groups, as seen in Figure 4. For the only coated samples it was about  $(17.1 \pm 1.7) \times 10^{-3} \text{ mm}^3$ , while for duplex samples the volume loss was  $(2.2 \pm 0.2) \times 10^{-3} \text{ mm}^3$ , which is almost the same value as the 10 N load tests. This means an increase of the wear in the only coated samples of about 2.9 times for an increment of only 7% in the Hertzian stress.

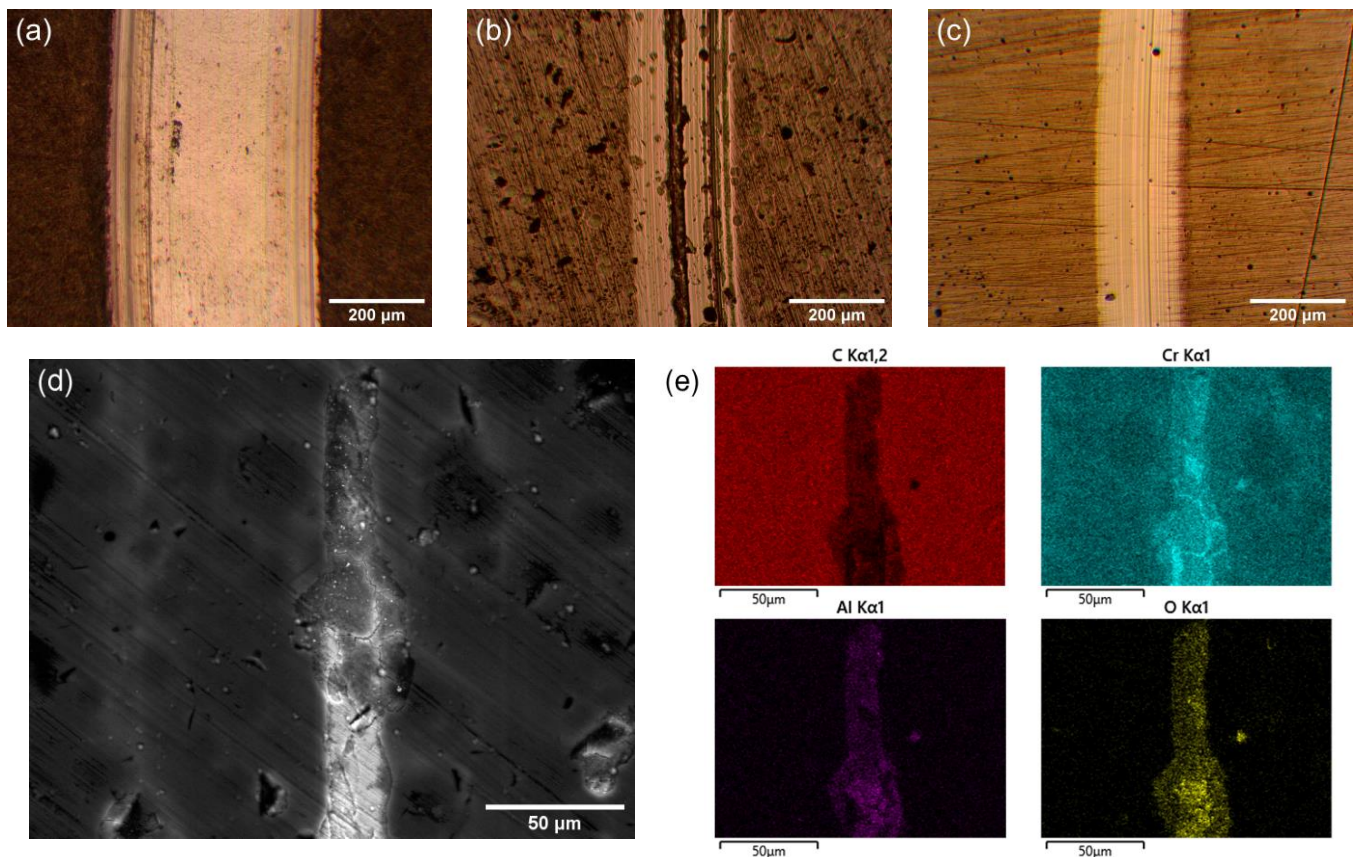
In the microscopic analysis of the wear scar, the nitrided sample, shown in Figure 5 (a), as expected, is wider than the coated samples in Figure 5 (b) and (c), and reached a depth of  $(12.2 \pm 2.1) \mu\text{m}$ . In the only coated sample, it is possible to detect an adhesion failure, represented as a deep scar in the middle of the track. The width of the whole wear track is similar to that in the duplex sample, but the maximum depth in the only coated sample is  $(3.3 \pm 0.2) \mu\text{m}$ , while for the duplex sample is only  $(0.5 \pm 0.1) \mu\text{m}$ . The wear track in the only coated sample is deeper than the thickness of the DLC coating but this is not the case of the duplex sample, where the top coating was barely worn by an abrasive mechanism.

In Figure 5 (d) and (e), a SEM micrograph with EDS mapping of the wear track of an only coated sample is shown. It is clear that the thin DLC layer was detached from

the rest of the coating, exposing the underneath Cr compounds layers, which have not good wear resistance for this predominant sliding conditions, given the high contact stress. In this region, traces of Al and O were also found, related to a rougher interaction with the alumina ball, which led to an increased wear in both parts of the tribosystem. In the 12 N load tests the same wear mechanism was noticed but with larger delamination zones, which explains the increased wear volume loss.

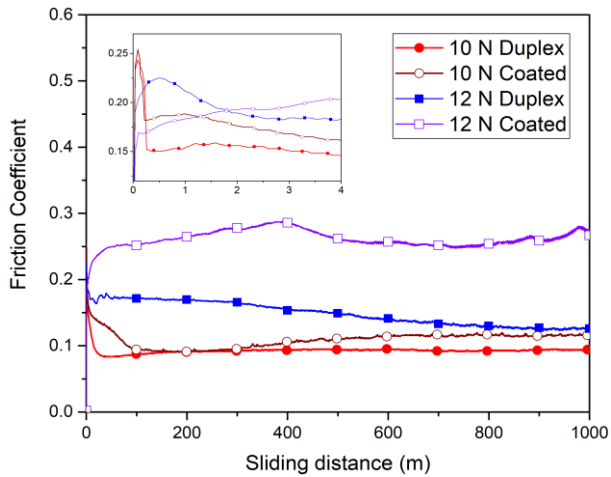
Regarding the friction coefficient, in the 10 N load tests and for the only coated samples it was  $(0.14 \pm 0.05)$ , and  $(0.12 \pm 0.02)$  for the duplex samples. This is a small difference considering that the friction coefficient of the untreated steel is about 0.65, which means a reduction of 80% in the coefficient of friction due to the DLC coating. This should be translated as an effective energy saving for components that are working under sliding contacts. In this relative motion, very small debris particles can be trapped in the interface or got adhered to the counterpart. When they are under high compression stress, they are sintered in solid and compact layers that can bear the load, they have graphitic characteristics and act as a solid lubricant between coating and counterpart, hence reducing the friction coefficient.

In the 12 N normal load tests, the friction coefficient of



**Figure 5.** PoD Wear tracks with 10 N load. Optical microscopy of (a) nitrided, (b) only coated and (c) duplex sample. (d) SEM image and (e) EDS mapping of only coated sample.

the only coated sample was about  $(0.26 \pm 0.04)$ , a higher value compared with the previous 10 N test, as it can be observed in Figure 6. The duplex sample had an almost identical friction coefficient as before, this is  $(0.13 \pm 0.02)$ , which is half the friction coefficient of the only coated sample tested in these conditions.



**Figure 6.** Friction coefficient from Pin-on-Disk tests on coated and duplex samples.

Looking into Figure 6 it is also noted that the running-in phase is slightly different when the load is increased. In the 10 N load tests, the friction coefficient shows a peak and then it goes down within the first sliding meter, reaching a steady state value in 100 m. On the other hand, the duplex sample tested at 12 N load needed over 3 m to reduce the first peak, reaching a steady state by the end of the test at nearly 800 m. The only coated sample tested at 12 N showed a different development, with no running-in peak but a constant increase in the friction coefficient, showing broad peaks along the test. All samples from this group showed the same behaviour, an increasing friction coefficient starting from a

certain point, meaning that in that moment an early adhesion failure occurred on the top DLC layer, exposing the chromium compounds underneath. When the delamination represents only a fraction of the wear track, as seen in Figure 5 (b), the remaining DLC can still transfer a graphite layer to the counterpart that could eventually cover this exposed chromium compounds with a thin layer of carbon lubricant, thus explaining the broad peaks and the reduction of the friction coefficient observed in these tests.

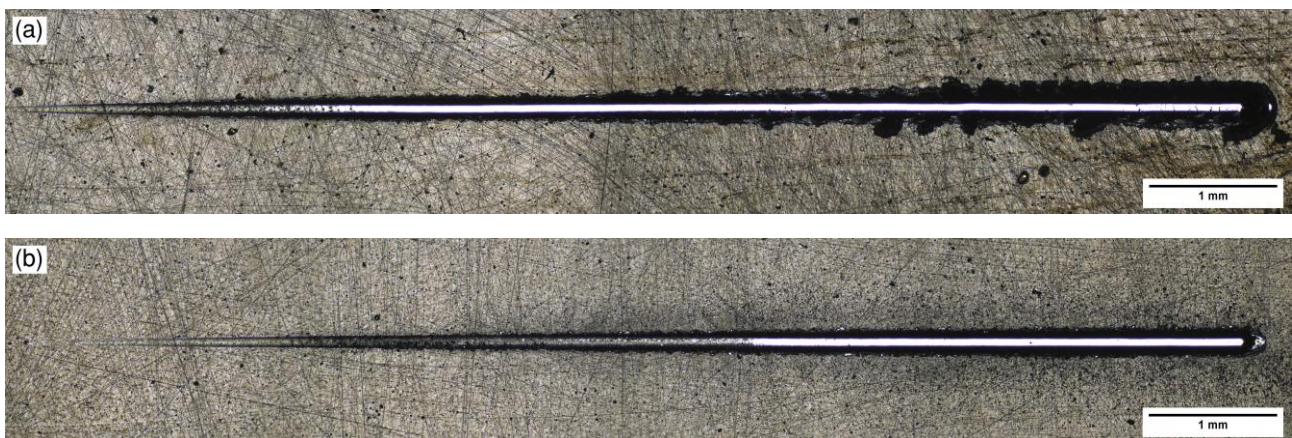
### 3.3 Adhesion

The variable load Scratch Test results are shown in the Figure 7 and the critical values are summarized in the Table 2, where it is clear to see that the full failure ( $L_{C2}$ ) of the only coated samples is at the same value where the duplex samples present their first cracks ( $L_{C1}$ ). The duplex samples have a load bearing capacity 2.5 times higher than the only coated samples. There is a noticeable increment in the plastic deformation for the only coated samples compared with the duplex, which have the hardness gradient to withstand the stress applied by the moving diamond tip. This behaviour is also evident with the maximum penetration depth of the scratch, which was  $(33.3 \pm 1.6) \mu\text{m}$  for the only coated sample, while for the duplex sample was  $(20.0 \pm 1.0) \mu\text{m}$ .

**Table 2.** Scratch Test Results.

Sample	$L_{C1}$ [N]	$L_{C2}$ [N]
Only Coated	$13.3 \pm 1.3$	$26.7 \pm 2.4$
Duplex	$27.1 \pm 0.6$	$63.3 \pm 4.1$

Regarding the Rockwell C indentation, there is an appreciable difference for the samples with the nitriding pre-treatment. The only coated samples have fracture and detachment of the top carbon layer, exposing the Cr compound layers. This is caused by a large plastic



**Figure 7.** Variable load Scratch Test of (a) only coated sample and (b) duplex sample.

deformation of the substrate due to the application of a high normal load. Meanwhile, the duplex sample had a better behaviour because it can hold its integrity, not showing any signs of plastic deformation or delamination around the indentation (not showed).

These adhesion results contribute to explain the behaviour of both types of samples in the pin on disk tests. When the maximum shear stress is located in the interface between the substrate and the coating or even below it, plastic deformation of the substrate occurs which develops in an increased stress and a consecutive disruption of the continuity of this interface causing coating delamination. The higher hardness in the nitrided sample and the hardness gradient through the core helped to manage this tensional state, avoiding an adhesion failure in the duplex samples.

#### 4. Conclusions

The multilayer coating is dense and homogenous, composed of tough chromium compound layers and has good tribological properties due to the hydrogenated amorphous carbon as the top layer.

The friction coefficient, due to this DLC top coating, is as low as 0.1, a typical value found in this kind of films, which in combination with the Cr(C,N) compounds, provides higher load bearing capacity and increases the wear resistance in sliding conditions.

Adhesion was **two times better** in the duplex samples, with ion nitriding as pre-treatment. This combination of treatments is determinant to improve mechanical resistance in coated steel components in severe wear conditions or under high contact stress. **Wear resistance was increased by a factor of three in the duplex condition when the highest contact pressure was applied on the tribological tests.**

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