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ASSESSMENT OF MULTIFUNCTIONAL COATING ADHESION: COMPARISON BETWEEN INDENTATION AND SCRATCH TESTS*

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Abstract

The adhesion of multifunctional coatings on soft substrates is of paramount importance in the tribological behavior of this important class of surface treatment. In particular, scratch and indentation tests have been extensively used in order to assess this property. In this paper, the adhesion of a-C:H diamond-like carbon films deposited on nitrided low carbon steel was evaluated by indentation and scratch tests. The coatings were produced by PECVD onto 1020 steel substrates with two different surface finishing: ground (Sq = 0.184 µm) and polished (Sq = 0.002 µm). Indentation tests using a Rockwell diamond indenter were conducted and the adhesion evaluated by measuring the spalling region on images obtained by using optical microscopy. The analysis of the spalling regions produced semi-quantitative results, eliminating the subjective qualitative analysis proposed by the standard method VDI 3198. In addition, scratch tests were performed using the same indenter and a comparison between the two techniques was established.

Keywords: Diamond-like carbon; Adhesion; Topography; Nitrided steel.

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1 INTRODUCTION

Diamond-like carbon (DLC) films have been used in the past decades due to, among other properties, their unique ability to enhance wear resistance and reduce friction in a variety of tribological pairs [1]. These films are mainly structured as amorphous carbon allowing the achievement of properties similar to those of diamond, such as: hardness, elastic modulus and chemical inertness [2]. Lack of adhesivity on DLC coated components has been reported since the early 90's and it is mainly attributed to the magnitude of the residual stresses normally formed during deposition processes [3-4].

The incorporation of strong carbides forming elements such as silicon in the interface has a beneficial result on DLC adhesivity, once it yields an improvement of the chemical component of the bonding [5]. It has been reported on the literature an increase on DLC adhesivity by the prior bombardment of the substrate with argon ions [6-7]. The treatment increases the roughness of the substrate leading to an improvement of the mechanical component of the bonding [6,8]. Morshed [9] suggests that, by optimizing bombardment conditions, it is possible to maximize adhesivity and minimize residual stresses, without having a significant impact on hardness.

Although there is an extensive literature on adhesivity improvement, the evaluation of this property is mainly still qualitative [10-12]. Among other tests, Rockwell-C indentation, described by the standard method VDI 3198, and scratch are the most common ways of assessing adhesivity of DLC films [10-14]. In this work, instead of comparing the morphological aspects of indentation tests with those proposed by the standard, a numerical comparison was possible by quantification of spalled areas through optical microscopy image analysis. In addition, scratch tests were performed using the same indenter and a comparison between the two techniques was established.

2 MATERIAL AND METHODS

To evaluate DLC adhesivity in different levels, two conditions of surface finishing were produced on 1020 steel substrate through metallographic preparation. The first condition named ground samples (GS) was obtained by grinding the substrate with SiC sandpaper firstly with mesh 120 followed by 220. The polished samples (PS) were produced by grinding the surface until mesh 1200 and then polishing with Al_2O_3 particles (1 µm and 0,3 µm diameter). The samples were then cleaned in ultrasonic bath with acetone for 20 minutes.

Since 1020 steel is relatively soft in comparison to DLC coatings, prior to the deposition the samples were nitrided in order to produce a ε rich (Fe_3N and Fe_2N) layer leading to sufficient mechanical support. A Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor was used to produce both nitrided layer and DLC coatings in a single batch. The hydrogenated amorphous carbon (a-C:H) films were formed using CH_4 precursor and a silicon rich interlayer was used to improve adhesivity of the films. Samples were sectioned and prepared to analysis in optical microscopy allowing measurements of thickness of the nitrided layer and DLC.

The characteristics of the chemical bonding of carbon atoms of DLC films were measured by Raman spectroscopy with an argon laser (characteristic wave length = 514 nm). The shift, as well as the intensity, of the graphite (G, $\lambda = 1580\ cm^{-1}$) and disorder (D, $\lambda = 1360\ cm^{-1}$) bands can be evaluated and associated with morphological changes in the film. It is also possible to estimate the atomic hydrogen content of the

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a-C:H films [2,15]. Also, nitrided samples, without DLC, were produced in order to evaluate the structure of support layer by x-ray diffraction (XRD), in which the diffraction peaks associated with the ε-iron nitride can be identified.

The topography of samples was assessed prior to nitriding and after DLC coatings with white light optical interferometry. The three-dimensional maps were analyzed with MountainsMap® Universal software using a Gaussian filter with 0.25 mm cutoff for all surfaces. The published studies relating topography of substrate with DLC performance normally use 2D amplitude parameters, such as *Ra* and *Rq*, which allow a good description for totally isotropic surfaces [7,16]. In this work, the 3D parameters shown on Table 1 were chosen to better represent the topography of samples.

Table 1. Description of topographic parameters

TYPE	PARAMETER	DESCRIPTION
Amplitude	Sq (µm)	Root mean square surface roughness
Hybrid	Sdq (µm/ µm)	Root mean square surface slope
Functional	Sk (µm)	Core roughness depth
Functional	Spk (µm)	Reduced peak height
Functional	Svk (µm)	Reduced valley height

The first method for estimating adhesivity of DLC films was the indentation test, according to the VDI 3198 standard. The indentations were made with a cone shaped diamond Rockwell-C indenter with 0,2 mm tip with 1470 N load. With such an extreme load, the substrate deforms and eventually the film delaminates [10]. The standard method suggests the comparison of the surrounding regions of indentations with six different patterns of failure leading to qualitative results. Aiming to improve the analysis, a new enhanced method is presented, in which the measurement of the spalled areas with image analysis is used to compare the adhesion of DLC films. To enhance the contrast between spalling and DLC surfaces a mild polishing was performed during 10 seconds with Al_2O_3 0,3 µm before image acquiring. Then, two different phases (spalling and DLC plus indentation) were quantified by the software AnalySIS ® (Figure 1).

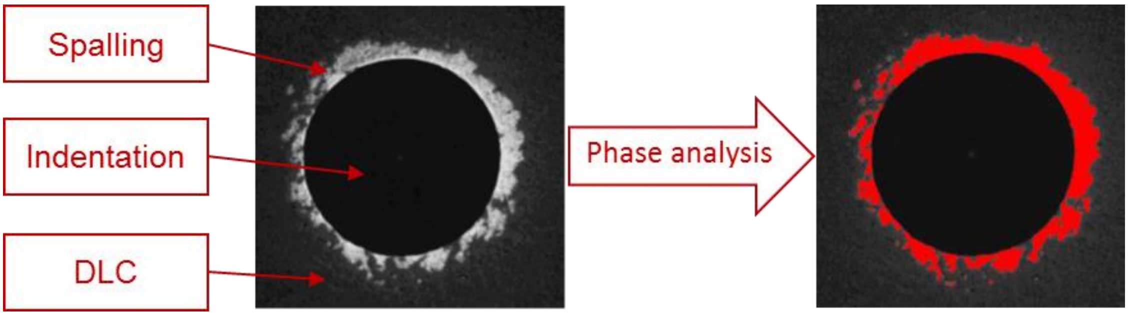

Figure 1. Spalling area measurement

To compare the results, scratch tests were conducted according to the standard method ASTM C 1624-05, in which the Rockwell-C indenter is used. In this test, a preload of 3 N was applied and linearly increased until 15 N. The loading rate and sliding speed were, respectively, 1 N/mm and 10 mm/min, resulting in 12 mm scratches. The scratches were then observed with optical microscopy to determine the location of the first adhesive failure located inside the track with exposure of the

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substrate (L_{c1}) [17]. Since the load increases at a constant rate, it is possible to associate a critical load with the failure position.

3 RESULTS AND DISCUSSION

3.1 Coating Characterization

In order to show the multi-layer coating morphology and measure the DLC and nitride layer thicknesses, the cross section of samples from each group (Ground and Polished) was analyzed after metallografic preparation (Figure 2) They presented thicknesses of 2,3 ± 0,2 µm for DLC layers and of 4,3 ± 0,5 µm for nitride layers.

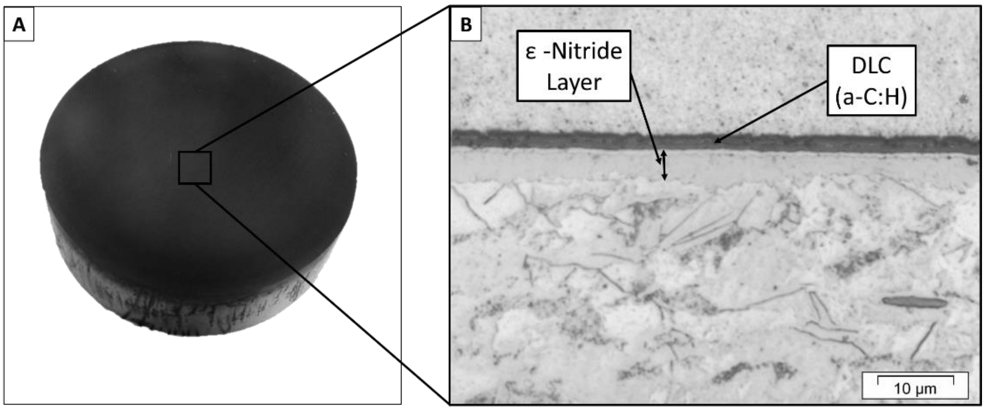

Figure 2. Aspect of the samples after DLC deposition (A). Cross section micrograph showing typical DLC and nitride layers thicknesses (2500x) (B)

Raman spectra of resulting samples were analyzed and both D and G bands were centered on ~1390 and ~1560 cm^{-1} for both groups of samples, typical values for DLC films. Using the methodology described by Casiraghi [15] the hydrogen content found was of approximately 50% at., however D and G bands were still visible and measurable (Figure 3).

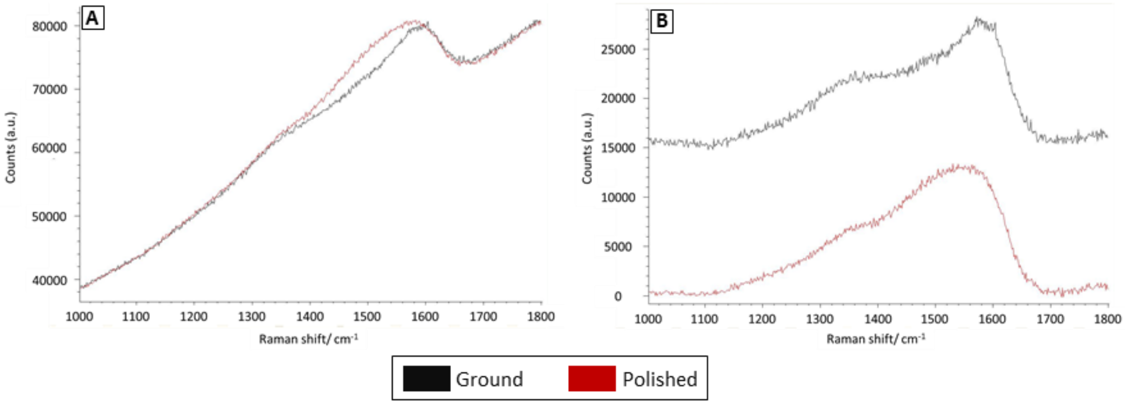

Figure 3. Raman spectra of a ground sample a polished sample. Untreated spectra (A), and after baseline extraction (B)

In addition, XRD analysis of the nitrided layer conducted for both GS and PS samples, as expected showed the presence of mainly ε phase (Fe_3N and Fe_2N) phase, with minor content of γ’ phase (Fe_4N) (Figure 4). A few low intensity α iron peaks associated with the substrate were also detected. These results are in accordance with previous studies of the group on the subject [18-20]. Also, no remarkable differences were found

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concerning polished and ground samples in XRD analysis, with only a minor increase in the γ' content for PS.

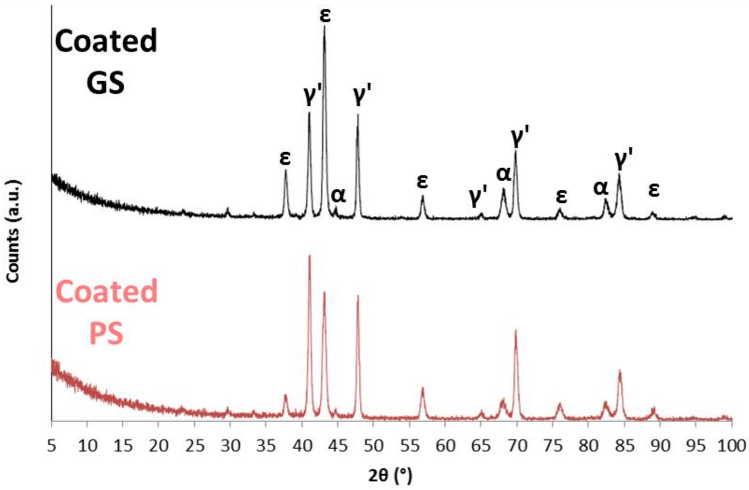

Figure 4. X-Ray difractometry for GS and PS coated samples, with similar results for x-ray diffraction analysis

3.2 Topography measurement

In Figure 5, the axonometric projections obtained from white light interferometry are shown for all conditions. It is possible to observe the different aspects of surfaces for polished and ground samples before and after the PECVD process, with a significant increase on the roughness as a whole. In the polished sample, for example, the full scale from the deepest valley until the highest peak was of 60.1 nm before treatment and of 2.75 µm afterwards. This phenomenon is related to ion bombardment during plasma processing [19,21].

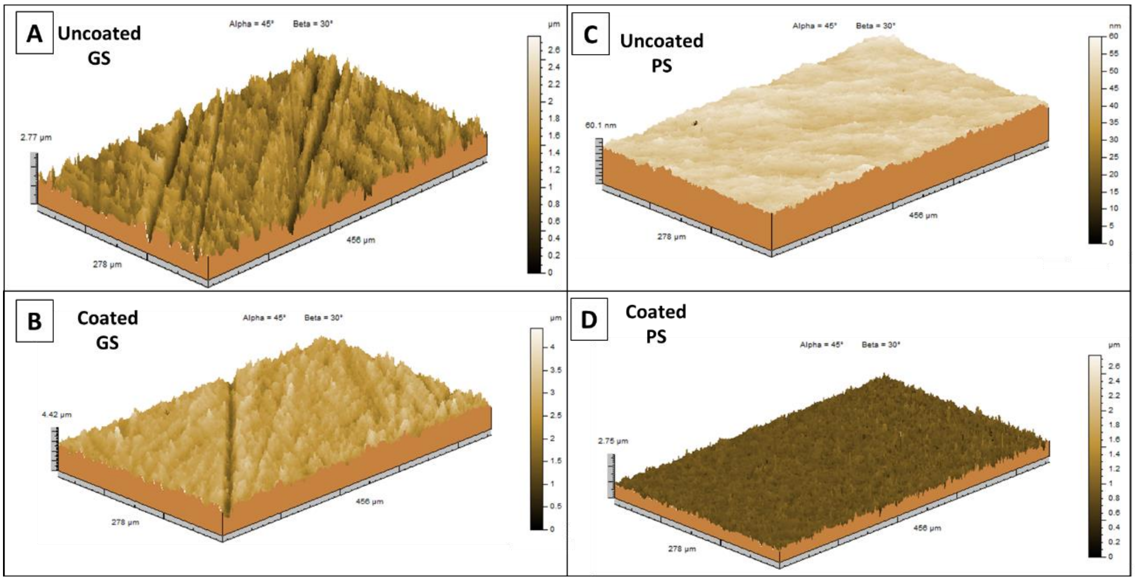

Figure 5. Continuous axonometric projections of surface analysis for Uncoated GS (A), Coated GS (B) and Uncoated PS (C) and Coated PS (D) The color scales are automatically generated with 0 (black) for the deepest valley until the highest peak of each surface roughness (white).

This increase of topographic parameters after the nitriding and coating processes for both polished and ground samples, notable in the axonometric projections, is displayed

numerically on Figure 6. This introduction of asperities and valleys on the substrate, if produced in proper intensity, can be benefic for mechanical anchoring of DLC, increasing adhesivity between layers [7].
The effect of ion bombardment during processing becomes clear by comparing the topographic parameters values of uncoated and coated samples, especially for polished samples, where the roughness of a nearly flat surface becomes comparable to the ground sample roughness (one order of magnitude increase). It is also noticeable an increase of steepness (Sdq), together with higher asperities (Spk) and deeper valleys (Svk) for both PS and GS after the coating process.

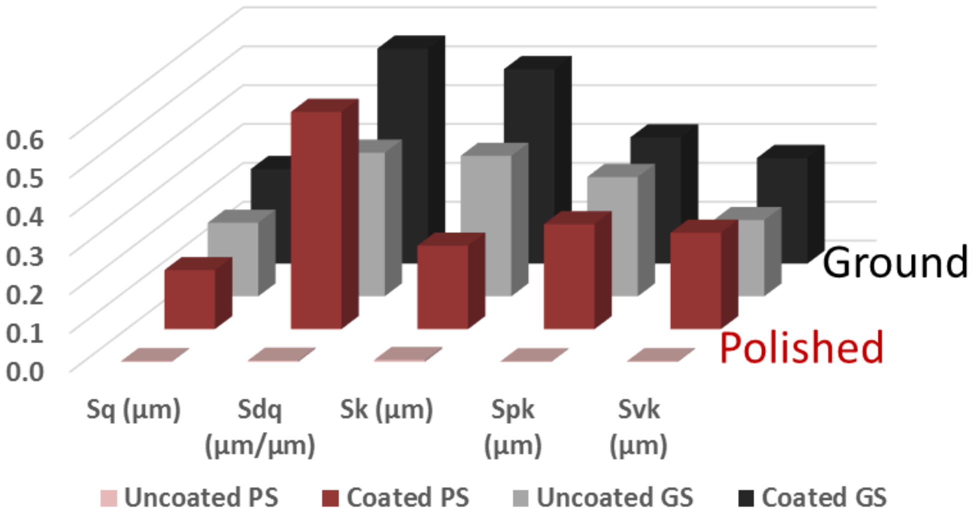

Figure 6. Topographic parameters average values for Uncoated and Coated PS and GS

3.3 Adhesion Evaluation

The spalled areas of PS and GS were compared in a quantitative way by using image analysis as an alternative to differentiate between samples with spalling on the surroundings of Rockwell C indentations. In Figure 7, images of polished and ground samples with typical aspect after indentation and mild polishing are shown. It can be pointed out that both conditions would be classified as HF5 or HF6 (non acceptable) according to the VDI 3198 standard. Furthermore, the results of comparison with patterns is not as accurate, once it depends on subjective analysis. The method provides a quantitative measurement that can be related to the adhesivity, allowing a statistical approach on comparison and conclusions on the subject. Ground samples exhibited significantly larger spalled areas as polished samples, as presented on Figure 7. Therefore, a difference in the initial topography led to different adhesivity behavior, which would not be so clearly detected by comparing the spalled regions with the patterns proposed by the standard method.

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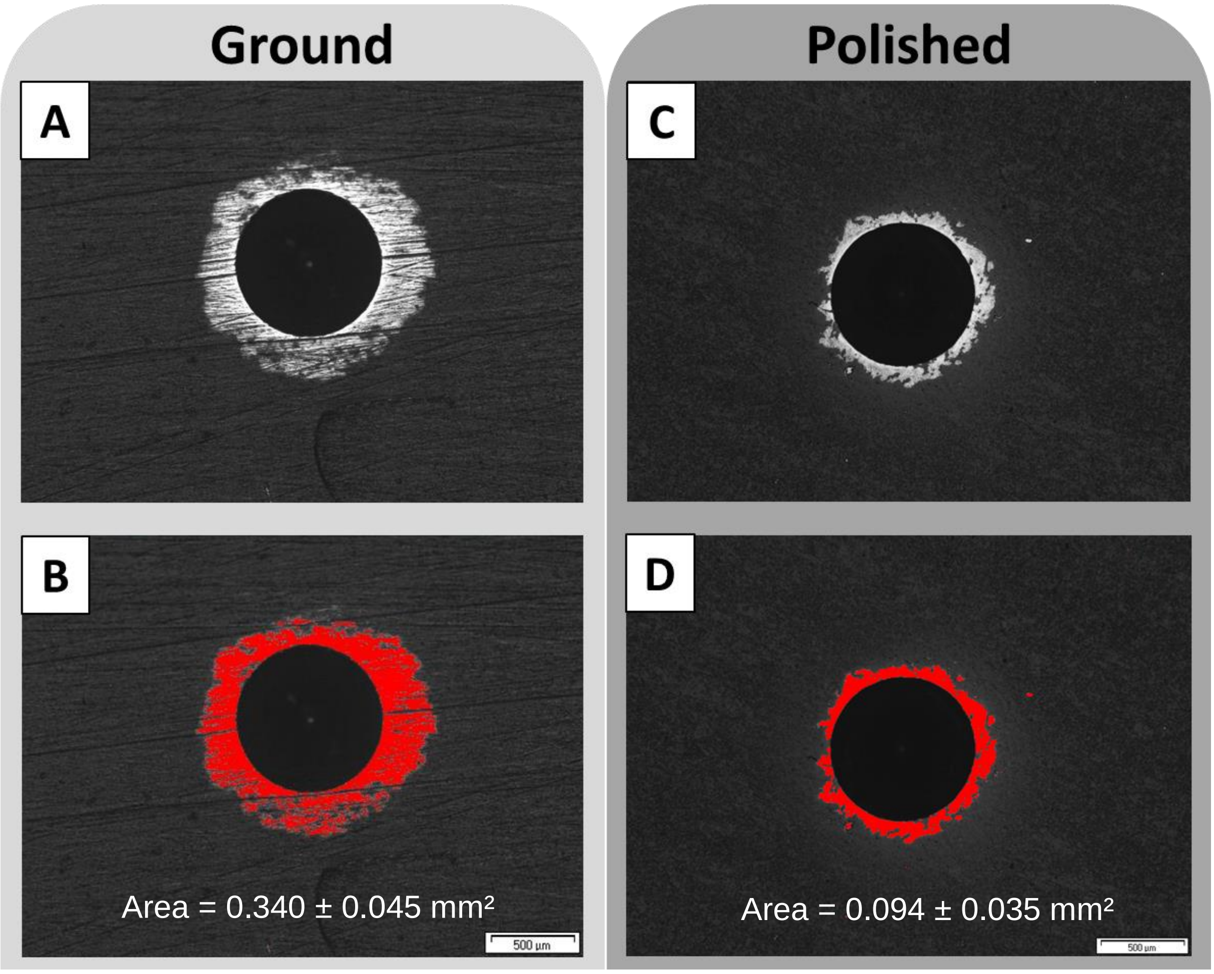

Figure 7. Examples of images used in the image analysis for Ground (A, B) and Polished (C, D) samples, red regions were the ones accounted as spalled regions (100x magnification)

In the sequence, scratch tests were performed to evaluate in a quantitative way the adhesivity of DLC coating on Polished and Ground samples. During the tests both normal and tangential loads increased linearly, giving a nearly constant friction coefficient during tests. A typical behavior observed during the scratch tests is displayed on Figure 8, via an optical micrograph of the scratch with the corresponding normal and tangential load vs. sliding distance graph. For this testing condition no total delamination of the coating was observed, therefore a more suitable way of comparing the results is the first adhesive failure inside the track (L_{c1}). However, the method for determining the first failure position still needs improvement, since sometimes it is hard to differentiate pre-existent flaws of film from the failures caused during testing. Isolated small defects on the beginning of the test were considered as pre-existent flaws, since these had the same aspect of the ones present on the surroundings of the scratch (Figure 8).

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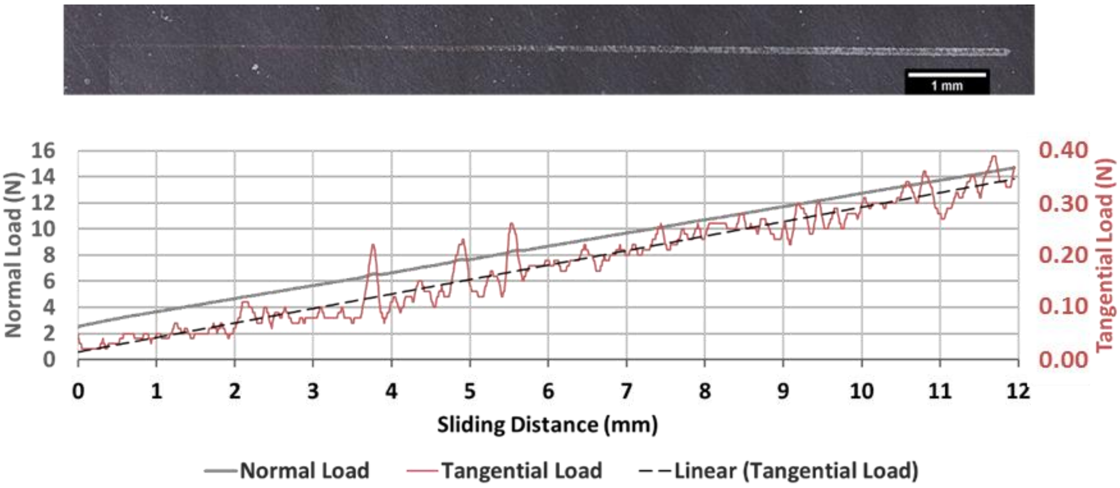

Figure 8. Optical microscope image of scratch in scale with Normal and Tangential Loads vs Sliding Distance graph

Comparing the results of indentation spalled areas and scratch tests critical loads is possible to notice a trend displayed in Figure 9. It can be seen that higher critical loads exhibited lower spalled areas, resulting in a better adhesivity response. It is also possible to point out that the ground samples exhibited an overall poorer adhesivity performance.

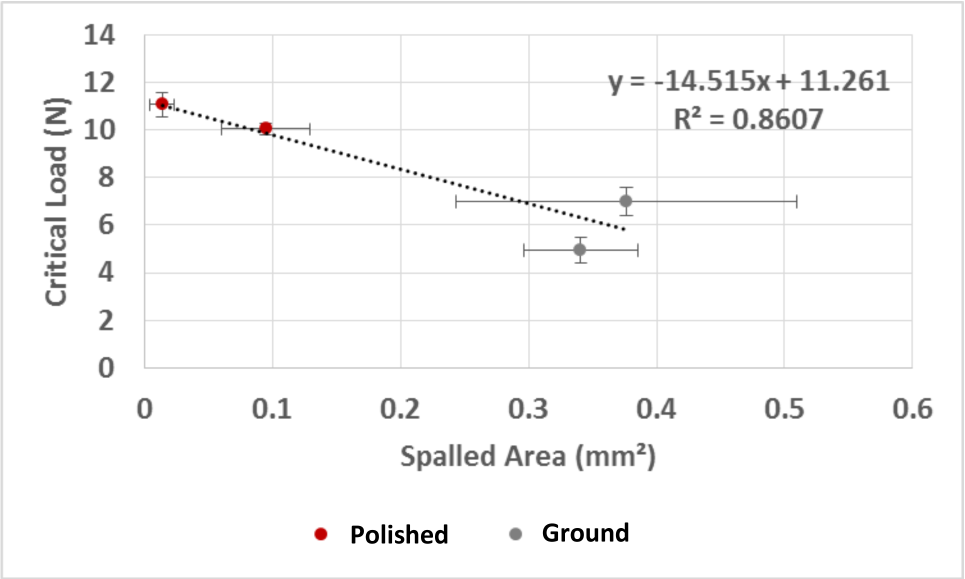

Figure 9. Summary of results comparing spalled areas and critical loads found for samples of both ground samples (GS) and Polished Samples (PS).

4 CONCLUSION

No significant differences on nitrided ε layer depth and morphology was observed between tested surface's conditions, however a small increase in γ' peaks intensity was observed for polished samples. Raman spectra for DLC films were equivalent for both conditions. As expected, an intense topography change was observed due to nitriding and DLC deposition by the PECVD, especially on polished samples.

Regarding the enhanced method to the VDI 3198 standard proposed by this study, better comparison could be drawn from measuring the spalled areas rather than comparing them with patterns. Finally, the comparison of spalled areas and critical

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loads (L_{c1}) from scratch tests showed a coherent response, where films with higher critical loads presented lower spalled areas. Ground samples presented an overall poorer adhesivity response.

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