Tribo-mechanical properties of hard hydrogen-free DLC coatings prepared by magnetron sputtering

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Abstract

The present paper presents data on the properties of hydrogen-free Diamond Like Carbon (DLC) films deposited by magnetron sputtering at low temperature. A magnetron magnetic configuration optimized for C-based compounds combined with pulsed plasma excitation modes is used to achieve hardness values in the range of 35GPa, even though no bias was applied during the C layer deposition.. For metallic substrates, such as M2 HSS steel commonly used in cutting tools, a Ti HIPIMS pre-treatment is used to enhance DLC film adhesion to the substrate. Rockwell-C adhesion and critical load on nano-scratch tests show that the films exhibit excellent resistance to delamination. Tribo-mechanical properties, such as micro-hardness, elastic modulus, friction coefficient were also measured.

Introduction

Diamond-Like Carbon (DLC) coatings have been recognized as one of the most valuable engineering tribological surfaces for a variety of industrial applications [1]. The low friction and chemical stability has benefited certain applications, such as tooling for manufacturing processes (drilling, milling, punching, forming, molding), engine components (valves, tappets, camshafts, fuel injectors, bearings), glass industry, razor blades, biomedical and microelectronics. Among its properties, DLC has good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear [2]. In addition to some of these properties the decorative aspect of DLC coatings has increased the demand of DLC coated components [3-4].

Experimental

Substrate pre-treatment and DLC Coating deposition

The DLC deposition tests were carried out on a single vacuum vessel with two Gencoa's rectangular 40x10cm^2 magnetrons mounted with WC and Graphite targets. A third circular 2" N4E cathode with a Ti target is used for the HIPIMS substrate pre-treatment. The magnetron magnetic configuration is optimized for C-based compounds, that combined with pulsed plasma excitation modes allows ion assistance during C-based film deposition without the requirement of substrate bias [5]. The schematic configuration of the magnetics and a picture of the obtained plasma are shown in Figure 1. This result has implications for the development of hard coatings on insulating substrates For the deposition of both the WC compliant and the DLC layers, a N4E DC-pulsed up-to-150kHz power supply with enhanced voltage reversal characteristics was used [6]. The deposition time for the WC was 15min, while for the DLC layer was 90min, in order to achieve films in the range of 0.5 µm thickness. Scanning and Transmission Electron Microscopy images of the deposited heterostructures are shown in Figures 2 and 3.

As shown in the literature, coatings deposited after HIPIMS pre-treatment with ions such as a Cr, W or Ti exhibit superior adhesion compared to pre-treatments in Ar glow discharge or cathodic arc environments [7-8]. The use of metal ion bombardment for surface cleaning provides intense mixing in the near surface region, preserving the substrate interface crystallinity and giving rise to good adhesion strength between the substrate and the deposited film. In order to sputter clean the substrate surface and to "implant" Ti metal ions, two different hipV 6kW HIPIMS power supplies (hipV AB, Stockholm Sweeden) [6] in master-slave configuration were used. One power supply was used in order to establish the HIPIMS cathode discharge while the second power supply was responsible for maintaining the substrate bias voltage during the high current intensity peak of the HIPIMS pulse. The Ti HIPIMS discharge was operated at a pressure of 6mTorr with a peak target voltage of -550V, a frequency of 50Hz and a pulse width of 100 µs for 15min. As shown in the literature, a higher peak current increases the amounts of multiply charged Ti ions, and thus the substrate etching is more effective [9]. The peak current at the magnetron was 100A for all the experiments, giving rise to a peak current density of 5A/cm^2. The average power was limited to 250W for the 2" cathode. The target current and voltage waveforms recorded at the Ti magnetron discharge are shown in Figure 4. The substrate was biased the previously mentioned power supply with a -575 V peak voltage and current densities in the range of 150mA/cm^2.

All studied samples were deposited on M2 HSS and AISI 304 stainless steel substrates. Coupon sizes varied from 10 mm x10 mm x 2.5 mm to 30mm x 30 mm x 2.5mm coupon size. The larger size samples were used in order to accommodate pin-on-disc tests. The surface of the steel coupons was mirror-polished to surface roughness of Ra 0.05um. All coupons were ultrasonically cleaned in acetone and isopropyl alcohol baths for 15 min, and were then blown dry with nitrogen.

Adhesion and tribomechanical tests

Nanoindentation experiments were used to evaluate hardness and Young's modulus of the coatings. Coating adhesion was tested with Rockwell-C indentation and nano-scratch adhesion methods. Both nanoindentation and nanoscratching were performed using the Hysitron TI950 indenter. Hardness and Young's modulus were obtained using a sharp Berkovich indenter to peak loads of 2, 7 and 12 mN with 10 repeats for each load following ISO 14577-4 recommendations. Nanoscratch tests were performed with a conical probe of 5 µm radius. The nano-scratch procedure involves three sequential scans (initial topography-scratch-final topography). In the initial scan the load applied is low (0.1 mN) along the track. Once the topography is extracted a progressive load is applied up to 500 mN at a constant rate of 2.5 mN /s. Finally, topography was reassessed with a final scan at 0.1 mN. Five scratches were done on each coating with adjacent tracks separated by 200 μm. By observing the topography, it was possible to determine the onset of delamination and the critical load at the point where residual depth was no longer zero.

Daimler-Benz Rockwell-C test was performed in order to evaluate the film adhesion level. By applying a 150 kgf load with a diamond cone indenter the adhesion of coatings is classified from HF1 to HF6 according to the level of cracking or coating delamination around the indent [10].

To study the friction and wear of coatings a pin-on-disc tribometer was used. All tests were carried out in accordance to ASTM G99 standard [11]. A tungsten carbide ball with 6 mm diameter was loaded up to 10N. Rotation rate was 200 rpm along a 14 mm radius track. The test duration was 1 hour at room temperature.

Results and discussion

Adhesion and tribomechanical tests

Figure 5 shows the results from the Rockwell-C tests of the DLC deposited samples. On the left, an optical image of a WC-DLC heterostructure deposited onto a M2 HSS substrate previously etched with an argon glow discharge [Figure 5, left] is shown. The resulting indentation can be identified as the adhesion strength quality HF5. The DLC coating shows large delamination around the crater related to the poor adhesion of the film to the substrate. On the right, an optical image of a WC-DLC heterostructure deposited onto a M2 HSS substrate etched under HIPIMS plasma conditions and Bias [Figure 5, right] is shown. No visible failures around the indentation crater are observed, and can be identified as adhesion strength quality HF1.

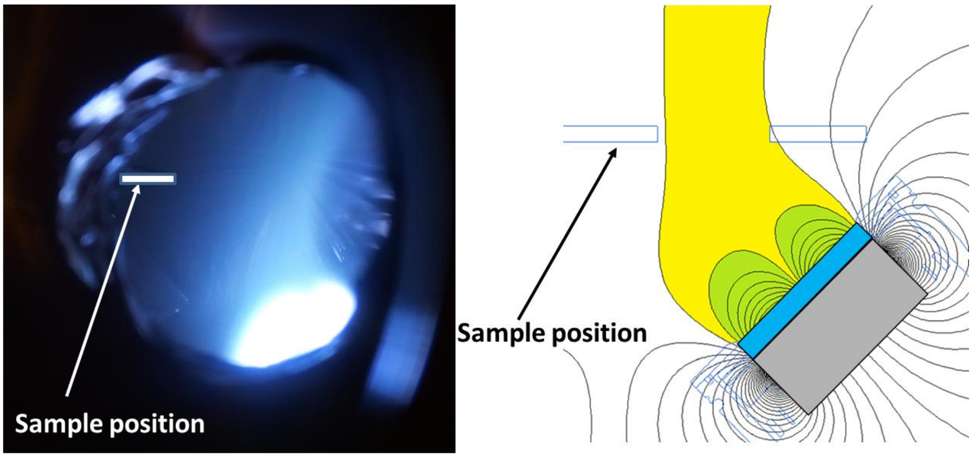
The nanoscratch measurements on heterostructured DLC also confirms a good degree of adhesion. A sub-surface interface weakening can be observed under optical microscopy (see Figure 6).

Figure 7 shows a measurement of the hardness as a function of depth for a 0.5μm WC-DLC heterostructure deposited on a M2 HSS substrate. A hardness value of 35GPa was obtained, taking into account that the values obtained at an indentation depth of 10% of the film thickness provide is a good estimation of the coating hardness.

Pin-on-disc test results can be seen in Figures 8 and 9. Figure 8 shows the comparative images for DLC coated and uncoated substrate. Strong adhesive wear can be observed on the uncoated substrate, while the coated substrate shows a very limited wear of the coated surface. Figure 9 shows the evolution of the friction coefficient during the pin-on-disc test. A coefficient of friction (dry conditions) on around 0.15 was obtained.

Dynamic multiple impact tests were conducted with 5 different increasing acceleration loads from 5 to 30mN are shown in Figure 10. The loading and unloading cycles for nano-impact tests involved linearly loading the specimen to full load in 1 sec and then releasing 100% of the test load in 1 sec with zero hold time at the peak load. Each test was conducted for a total of 1200 fatigue cycles at the same location of the specimen surface. As shown in Figure 10, no DLC coating failure or fracture is observed under different applied loads (increasing from 5 to 25mN). At 30 mN a possible sub-surface interface weakening could be observed, however even at that load no coating delamination was observed.

Figures



Proprietary technology: Patent application number GB1605162.5

Figure 1: Picture (left) and schematics (right) of the plasma configuration for the deposition of the C-based layers.

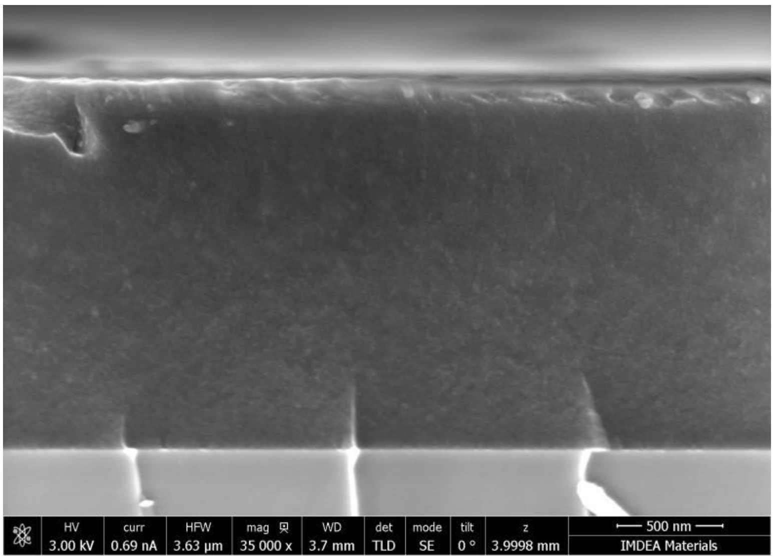


Figure 2: SEM image of the deposited DLC onto Silicon without Ti metal interlayer. Dense DLC coating and low coating stress can be appreciated from the SEM cross section.

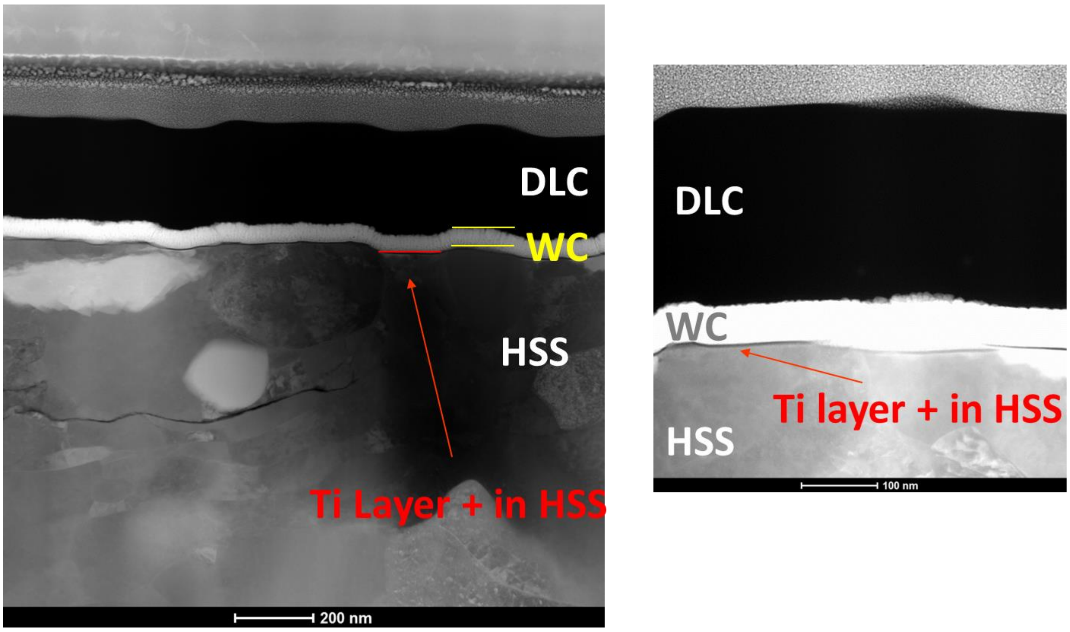


Figure 3: TEM images of the deposited layer stack, consisting of Ti-WC-DLC. The substrate was previously HIPIMS pre-treated with Ti. The substrate presents a degree of Ti mixing within the steel structure. This interface quality favours a strong adhesion of the coating heterostructure.

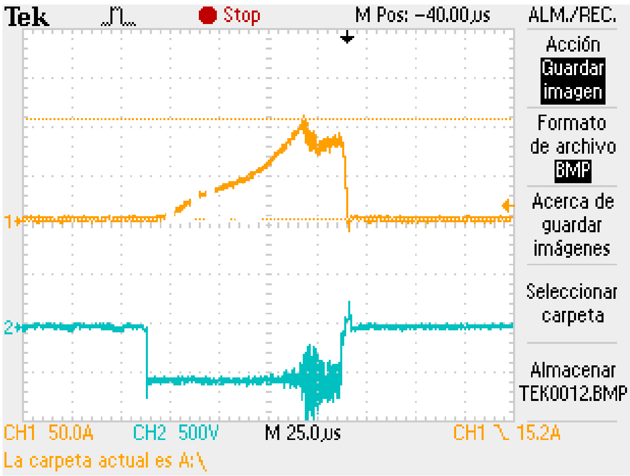


Figure 4: Target current (up), target voltage (down) waveforms recorded at the Ti magnetron discharge during the substrate pre-treatment.

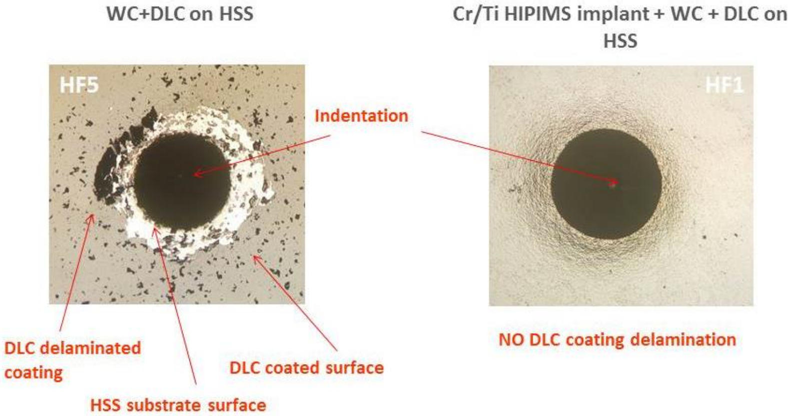


Figure 5: Optical micrograph of two different samples deposited with different substrate plasma pre-treatment. (left) HF=6, when an Ar glow discharge established with a DC-Pulsed 40kHz power supply is used to clean the substrate (b) HF=1, when the gas and metal ions are generated by an HIPIMS discharge in the cathode and a second synchronized HIPIMS power supply is used to maintain the DC voltage value at approximately -600V during the current impulse.

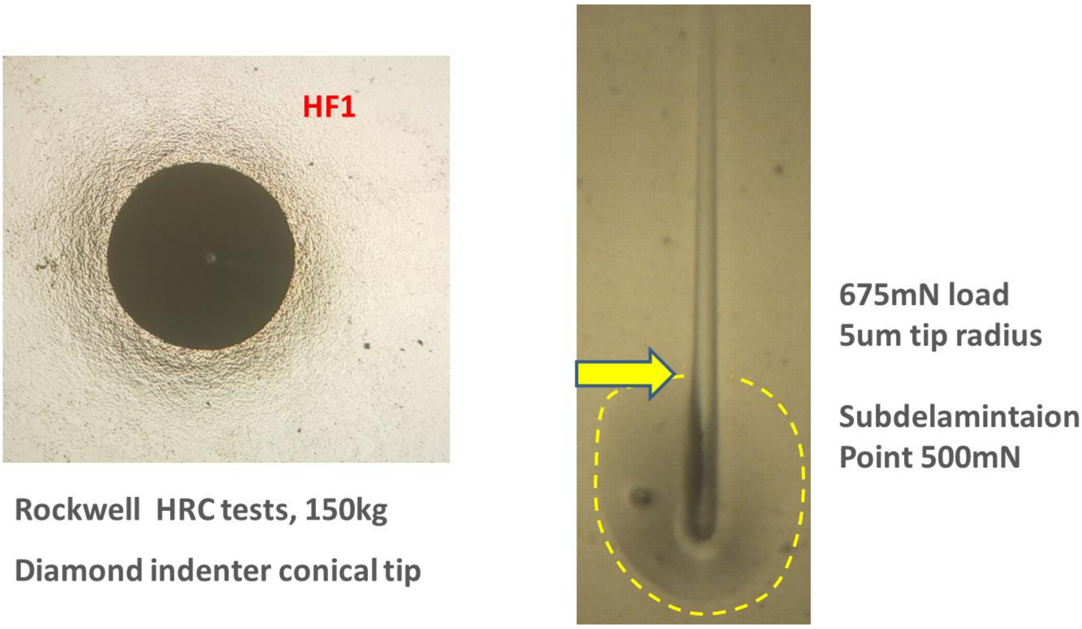


Figure 6: Daimler-Benz Rockwell-C test on DLC heretostructure (left) showing a high adhesion level (HF1). The right hand side image shows the nanoscratch on the same DLC coating heterostructure. Although, no complete delamination was achieved during the scratch test, what could be observed was a sub-surface interface weakening for loads higher than the 500mN region.

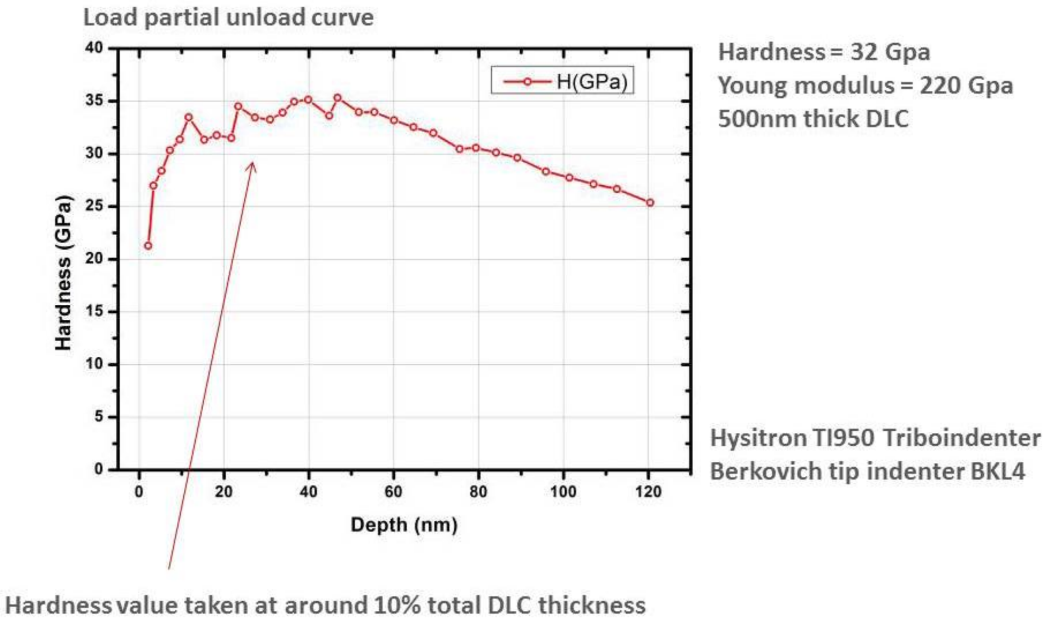


Figure 7: Berkovich nanohadness values as calculated during the indentation process. A 35 GPa hardness would be the representative value of the coating hardness.

Figure 8: Optical micrograph of the DLC coated (left) and uncoated (right) stainless steel substrates after the pin-on-discs test. The DLC coated sample does not show visible failure, while the bare substrate shows clear evidence of adhesive wear.

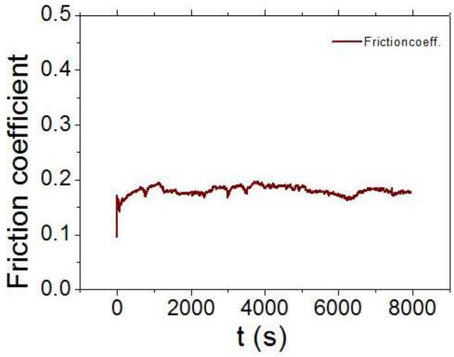


Figure 9: Evolution of dry friction coefficient of DLC coated AISI 304 stainless steel coupon against a tungsten carbide ball in the pin-on-disc test (10 N load, 200rpm, 14 mm radius track). The test duration was 150min at room temperature. Low and constant friction coefficient value of 0.15 is measured

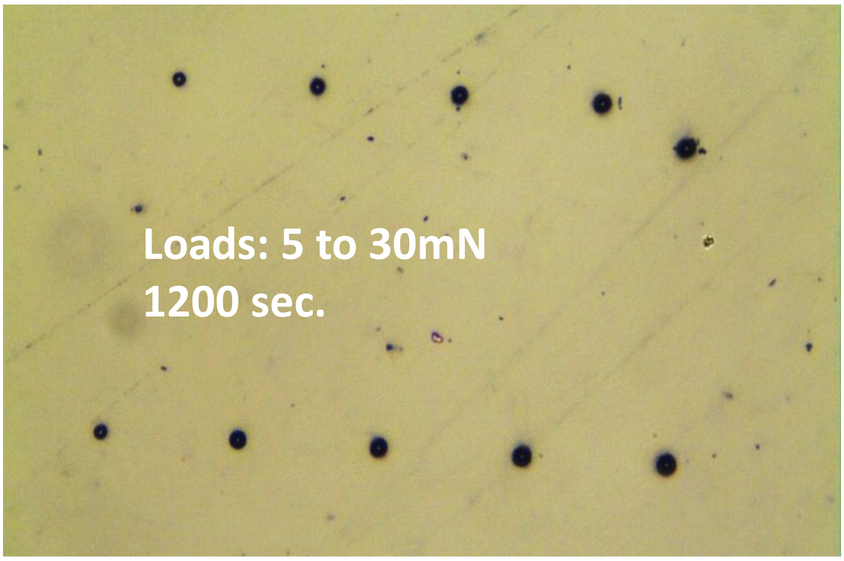


Figure 10: Corresponding optical micrograph of DLC-coated M2 HSS steel substrates after multiple impact tests. No DLC coating failure or fracture is observed under different applied loads (increasing from 5 to 30mN).

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