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TRIBOLOGY BEHAVIOUR OF CARBON-BASED COATINGS DEPOSITED BY PLASMA ENHANCED TECHNIQUES

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Abstract. *Tribology has been a problem with the global industrial scenario. Some billions of dollars are lost every year arising for this, United states show a study that 2% of his gross national product are lost , as well as England and Germany that lost 1% and 2.5% of GNP respectively. The carbon-based coatings could be an alternative to mitigate wear and improve lubrification in this scenery. The oil and gas industry has suffered from this problem, leading impurities and containing the oil. As a result leaks and corrosion damage this industry sector. In this project, the goal is to investigate the tribology behavior of the carbon-based coatings, deposited on AISI/SAE 4140 steel, obtained by three different deposition technique: PIID (Plasma Immersion Ion Deposition), HiPIMS (High Power Impulse Magnetron Sputtering) and PIID+PEMS (Plasma Enhanced Magnetron Sputtering). Nitrided and non-nitrided samples were investigated to compare the three different techniques. Adhesion evaluation and characterization of this DLCs were investigating too.*

Keywords*: Tribology, DLC, HiPIMS, PEMS, PIID, Carbon-based coatings.*

1. INTRODUCTION

Diamond-like carbons are a class of carbon materials that have shown properties that ranges from diamond-type to graphite-type (Lin et al., 2014). The key issue to obtain suitable properties of a specific application is to design a deposition process in which the sp^3 (diamond type), sp^2 (graphite type) and sp^1 (hybridized binding) bindings can be tailored (Robertson, 2002). The amount of each bonding can determine the type of DLC. DLC films of a-C:H type (amorphous carbon hydrogenated) typically have fractions less of 50% of sp^3 bonds and the a-C films can contain 85% fractions of sp^3 bonds or more. The hydrogen amounts can be less of 1% and up to about 50% of H (Grill, 1999). Carbon-based coatings are characterized by high hardness, high elastic modulus, high wear resistance, but also by high internal stresses.

Various techniques are used to DLC depositions. Amongst them, its mentioned: cathodic arc evaporation (CAE),ion beam deposition, magnetron sputtering, plasma enhanced chemical vapour deposition, pulsed laser deposition (Vetter, 2014).

The variety of deposition techniques make DLC be a good option for various application in industry, not only for scientific researches. DLC films have been used for optical, electrical and biomedical applications but new areas have been studied. Engineering applications such as micro pumps, micro motors, micro mechanical assemblies and micro tweezers need good tribological properties to works well (Grill and Patel, 1993). The carbon-based coatings are knowed by your low friction coefficient and this can be explained by a Liu, Erdemir and Meletis research in 1996 that show that outstanding hydrogen and oxygen bonds on the surface of the DLC reduce the possibility of bonding between the surface of the DLC and the counterface. Thus this chemical adsorption between hydrogen and/or nitrogen and the formation of a graphitization in the sliding interfaces are explanations of the low friction of the DLCs.

In tribology tests in a-C: H films, the predominantly sp^3 bonds become sp^2 bonds (Nistor et al., 1994), this occurs around 450 ° C, when have a hydrogen detachment from the film, which causes the destabilization of the tetrahedral bonds that aid in the formation graphite type carbon (Nyaiesh et al., 1983).

2. EXPERIMENTAL DETAILS

Six samples of 4140 AISI steel with 5 mm of height and about 1 inch of diameter was quenching of 855°C, tempering of 600 °C, sanded and polished to apply the coating. Before coating, three samples was nitrided with a 5% of N_2 and 95% of H_2 gas rate, temperature of 600 °C and 650 V peak voltage for 4 hours. The nitriding process was did on Laboratório de Caracterização Microestrutural of PUC-PR.

The carbon-based coating deposited by three different techniques: HiPIMS, PEMS+PIID and PIID. Each technique used two samples, one nitrided and one non-nitrided.

In HiPIMS and PEMS+PIID process, the coatings were deposited in a magnetron sputtering system. A Ti metal target (99.95% purity) and a graphite target (99.5% purity) were used to deposit the adhesion layer and the coating, respectively. The chamber was pumped down to a base pressure below $5x10^{-4}$ Pa prior to all depositions. The samples were mounted on a double rotation holder (speed of 4 rpm) and were ion cleaned at a bias voltage of -120 V and a global dicharge current of 4.5 A generated by powering tungsten filaments ate 45A using the PEMS method. Once the substrate cleaned was finished, a Ti/TiN compositionally graded bond layer (300-500 nm) was deposited. After this, the tungstein filament were turned of and then, DLC coatings were deposited via different methods.

To the HiPIMS-DLC, the graphite target was sputtered by a mixture of argon and acetylene gas on a Cyprium^{TM} plasma generator, Zpulser Inc.. A 2000 µs pulse length. 40 A peak target current, 1150 V peak target voltage, 134 Hz pulsing frequency, and 26.4% duty cycle were used. The Ar and C_2H_2 flow rates were 240 sccm and 5 sccm, respectiviely. The total deposition time was 7 hours and the obtained coating thickness was around 5 µm.

To the PEMS+PIID-DLC, C_2H_2 was fed into the chamber with a flow rate of 250 sccm and a 0.67 Pa working pressure. A constant voltage of -650V, 100 kHZ amd 90% duty cycle was used on a Pinnacle plus, Advanced Energy, LLC. The total time deposition was 4 hours, and the coating thickness was 4-5 µm.

The base pressure in the conventional PIID-DLC was $5x10^4$ Pa. The substrates were cleaned using an argon glow discharge plasma generated by applying a negative pulsed voltage on the substrates at a pressure of 2.67 Pa. After cleaning the substrates, a SiC bond layer (about 200 nm) was firstly deposited by intrucing TMS gas (20 sccm) into the chamber. The pulsing frequency was 500 Hz and the pulse was 20 µs. Then, the DLC coating was deposited by introducing C_2H_2 (80 sccm) into the chamber. The total deposition was 2 hours and the coating thickness was about 4-5 µm.

The surface analysis was did with a TESCAN-VEGA3 scanning electron microscopy (SEM) with a spectroscopy energy dispersive, this test evaluate the porosity and possible failures on the film. A profiler was used to determine roughness values. The hardness test was did on a nanoidenter EQUIPAMENTO, with a Berkovich tip and multiple load. It used loads of 10 mN, 20 mN, 30 mN, 40 mN, 50 mN, 100 mN, 150 mN and 200 mN. Relative humidity was kept between 50 and 60 % during the experiment. The scratch tests was conducted with progressive load, from 1 to 60 N, and a scratch length of 3 mm were done using a Rockwell C diamond stylus (200 µm radius) on a Revetest Scratch Tester, CSM Instrumenters and following the standard test method C1624-05 (2015).

The tribology tests was did on a circular method using Al_2O_3 balls as a counterface material. The experiments were conducted at an applied load of 10 N at 1 cm/s and for a total sliding distance of 1000 m. The tests were carried out in laboratory with relativity humidity about 50% and at room temperature.

. All this tests was did on Microestructural Characterization Laboratory of PUC-PR.

3. RESULTS

The SEM analysis on surface of the coating did not show failures or big porosity on the film, the three deposition techniques showed a uniform film and in this analysis, the nitriding process did not show big improvements on the coating. For the roughness, the nitriding process presents little improvements for HiPIMS-DLC and PEMS+PIID-DLC, for PIID-DLC the rugosity increased with the nitriding process. The lower roughness is for PIID-DLC, followed by PEMS+PIID-DLC and then HiPIMS-DLC, as shown in Tab. 2.

Table 1. Roughness values of DLC deposited by three different techniques.

	NON-NITRIDED SAMPLES	*NITRIDED SAMPLES*
HIPIMS	0,077 µm	0,057 µm
PEMS+PIID	0,029 µm	0,010 µm
PIID	0,009 µm	0,018 µm

On the other hand, the nitriding process presents good improvements to the adhesion. Upgrades up to 30 N in the critical loads were seen. The figure 1 show the critical loads arising from the scratch test, did to analyse the adhesion of the DLC. Lc1 is characteristic of lateral cracks that appear at the beginning of the risk. Two type of failures occur on Lc2, like buckling cracks (characteristic of thin films) (ASTM C1624-2015) and wedding spallation (characteristic of DLC coating) (Pagnoux et al., 2015; Zawischa et al., 2016; Sharma et al., 2012). The Lc3 was the parameter used to determinate when broke the coating. In this critical load, the failure was determinate as gross spallation, when the substrate appear. HiPIMS-DLC showed the best results of adhesion, followed by PEMS+PIID-DLC and then PIID-DLC. The critical load values found on HiPIMS were very acceptable, seeing that the Lc3 for nitride samples was 57 N, a very near value of maximum load (60 N). Researches showed that HiPIMS have good results of adhesion on your properties (Hiratsuka et al., 2013). Hardness tests results in values between 7 GPa and 20 GPa, proving that this is an a:C-H DLC type.

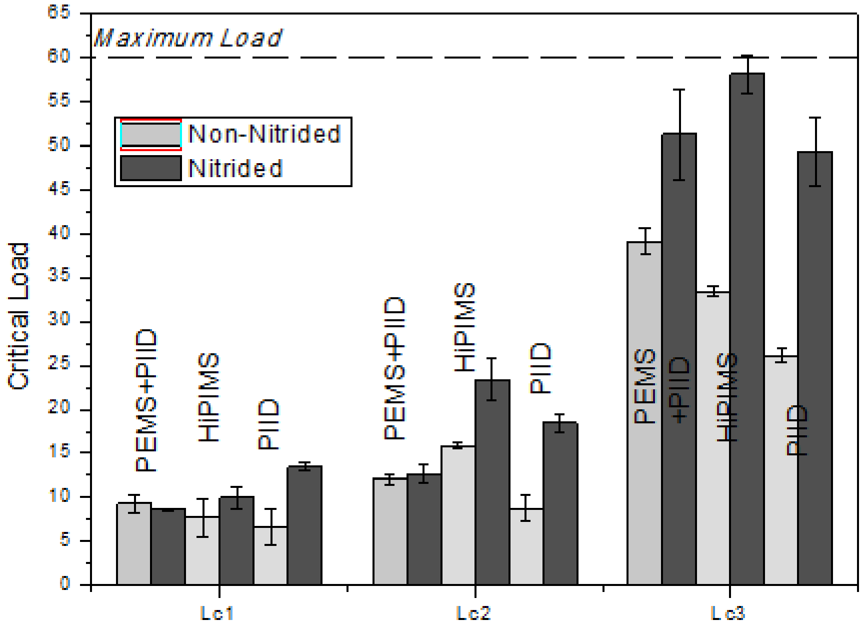
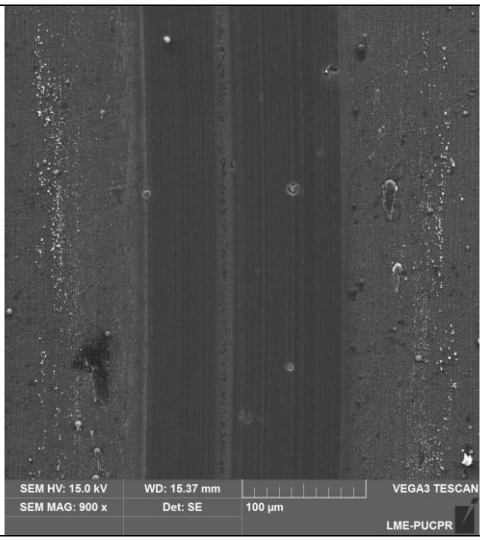
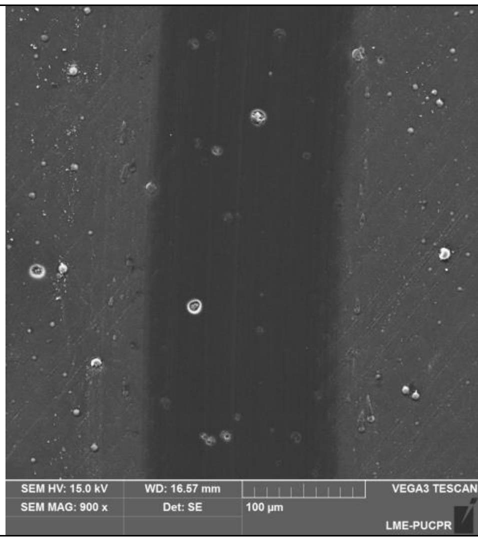
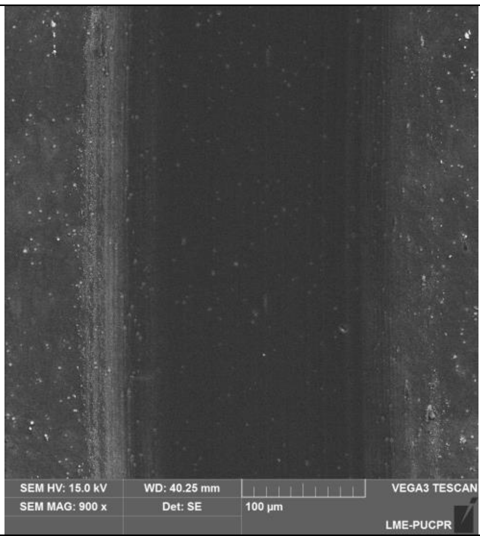


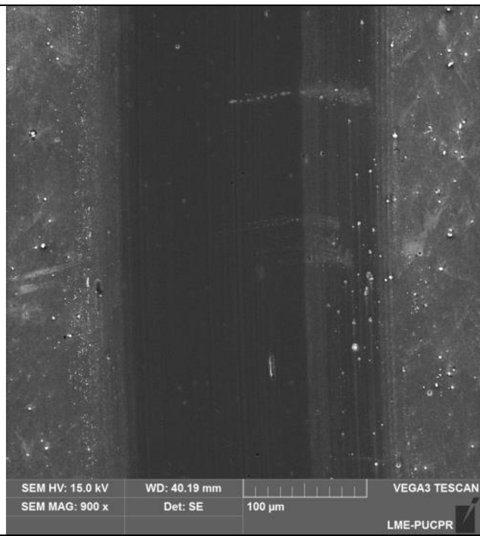
Figure 1. Critical loads of DLC coating deposited by three different techniques.

In tribology tests, although a large sliding distance has been used, the coating did not broke and the wear track region did not show big failures in all samples. As well as, nitriding process did not result in great improvements. All wear track had values between 150 µm and 210 µm of width, resulting in wear rate about 2.6x10^{-5} mm^3/N.m.

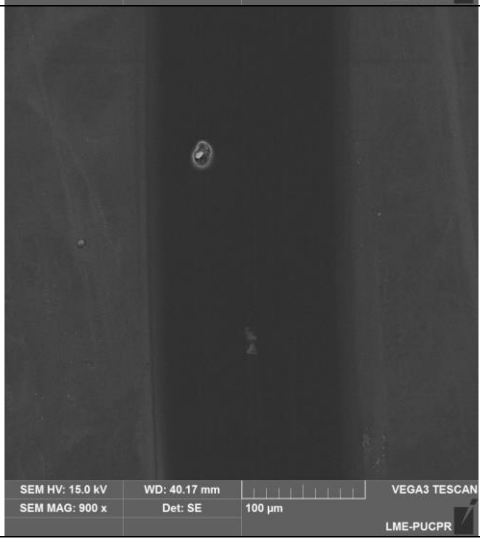
	Non-Nitrided	Nitrided
HiPIMS		

PEMS+PIID





PIID



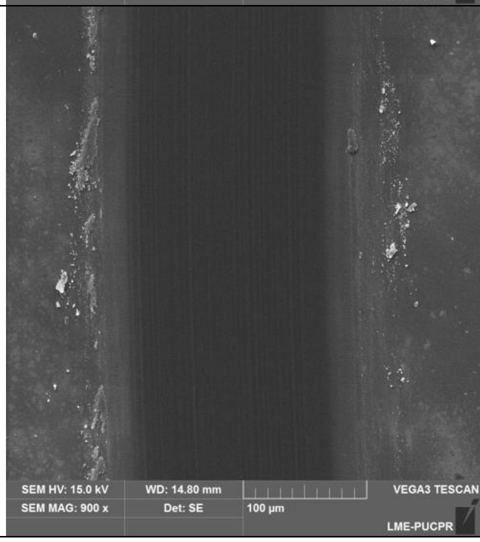
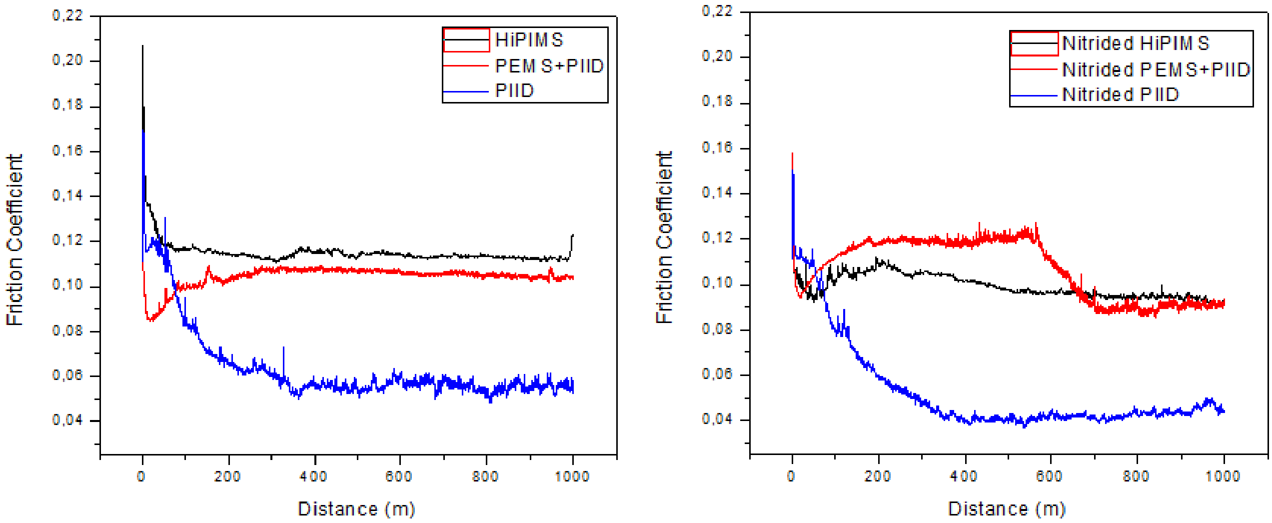


Figure 2. SEM images of wear track region of tribology tests on DLC coatings.

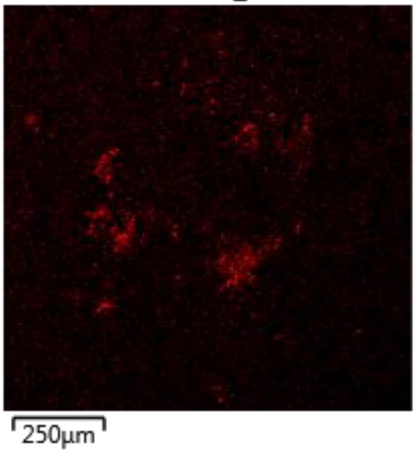
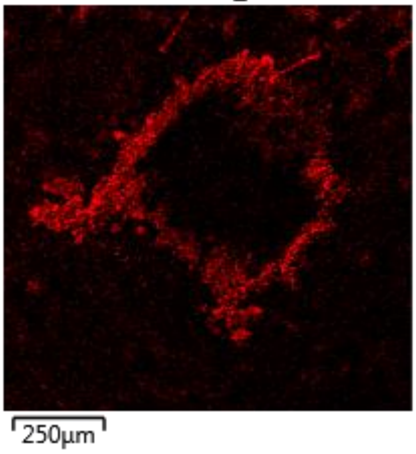
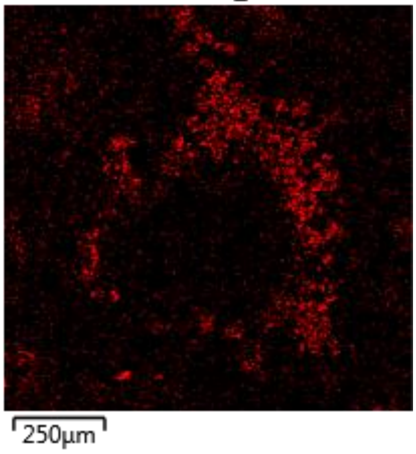
Fig. 3 shows the variation of friction coefficient (f) as a function of sliding distance. Is possible to note that in two cases, nitrided and non-nitrided samples have a period of decrease followed by a constant coefficient of friction (plateau region). The nitriding process results in a behavior of the less uniform friction coefficient curves, but the values of COF is lower on nitride samples, with exception on DLC by PEMS+PIID. The DLC coating is known by your lower friction coefficient, values in the range of 0.007-0.4 were found and were probe that the relative humidity can increase this values (Grill, 1999).

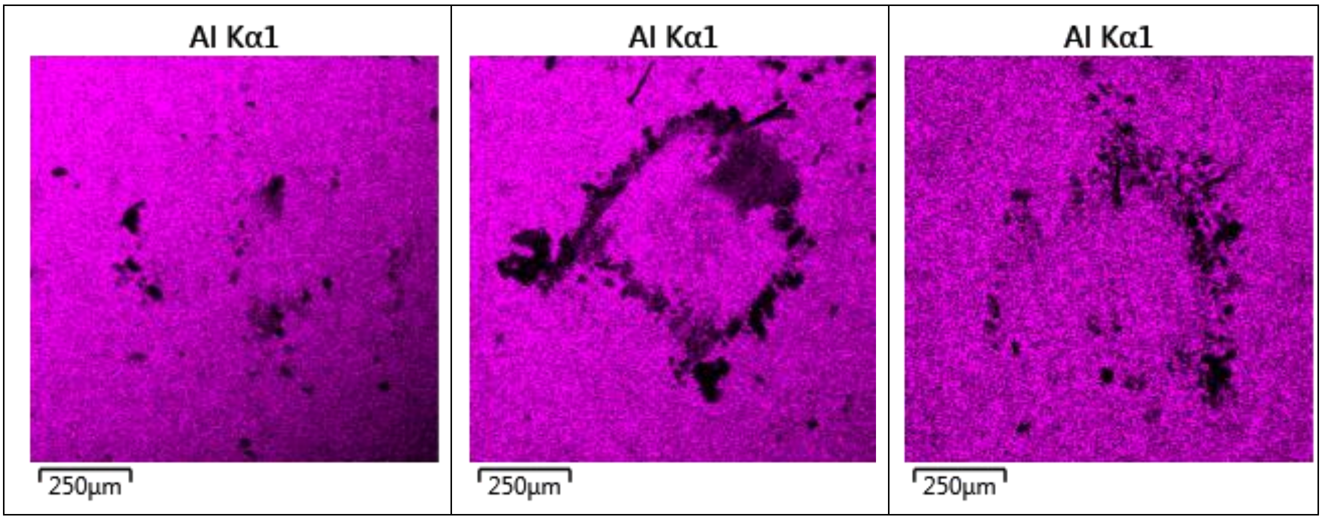


(a) *(b)*

Figure 3 - Friction Coefficient of (a) non-nitrided samples and (b) nitride samples.

In some researches (Grill, 1997) were proven that the tribological behavior of DLC is controlled by an interfacial transfer layer formed during the friction.The EDS analysis after testing showed that in all cases a carbon transfer layer was present on the surface of the counterface ball. The red color shows the carbon element, presents on DLC film and the pink color show the aluminum, presents on the counterface material. The carbon transfer layer was concentrated around the region that remained in contact with the samples. In the fig. 5 is possible to see that the DLC-PEMS+PIID had the biggest transfer layer, associated to the fig. 2, where the width of the wear track is the higher compared with the two other techniques. The larger surface contact area results in a higher initial rate.

HiPIMS	PEMS+PIID	PIID
C Kα1_2 	C Kα1_2 	C Kα1_2 



4. CONCLUSION

The purpose of this research in analyse three types of deposition techniques resulted in similar datas for the tests. The surface of the samples do not have big failures and them roughness is lower compared with other type of coatings. In this case, nitriding procces did not interfered in the results. For the adhesion evaluate, it was proven that HiPIMS-DLC support much more load then the other two techniques, nitrided procces helps on the good results too. The hardness tests prove that this samples are an a:C-H DLC type because have values between 7 and 20 GPa of hardness.

Tribology tests showed friction coefficients lower then f=0,1 and the carbon transfer layer occur in the counterface of aluminium. The wear track did not show big failures and the adhesion layer did not appear in all cases. Nitriding procces did not help in these tests.

In previous tests, it was seen that the DLC deposited by PIID have more quantities of sp^2 bindings, compared of the DLCs deposited by other two deposition techniques. This higher quantity of sp^2 bindings was reflected on the lower friction coefficient. The sp^2 bindings was characteristic of graphite, material auto lubricant.

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