



A DLC/diamond bilayer approach for reducing the initial friction towards a high bearing capacity

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ABSTRACT

Sliding contact mechanics is used to account for the net increase of the bearing capacity of high wear-resistant CVD diamond coatings when an outer layer of a DLC lubricant film is deposited on their top surface. Experimental results, namely the critical failure load, taken from reciprocating ball-on-plate tribological testing of such DLC/diamond bilayers, are on the basis of this statement. DC magnetron sputtering was used to grow thin DLC lubricant coatings (non-hydrogenated and hydrogenated varieties) on the top of CVD diamond films (microcrystalline and nanocrystalline types). The application of the von Mises maximum yield parameter ($\sqrt{J_2}$) criterion demonstrates to be an adequate method for designing low-friction and high-bearing capacity systems for high-demanding tribological applications. Calculation of $\sqrt{J_2}$ supports that the most significant increase observed on the coatings' bearing capacity (from 20 N to 60 N) takes place when microcrystalline diamond is coated by hydrogenated DLC that decreases the initial friction coefficient peak (from 0.76 to 0.41).

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1. Introduction

Chemical vapor deposition (CVD) diamond is known for its outstanding physical and chemical properties such as an extreme hardness, high wear resistance and chemical inertness, being usually used for high demanding tribological applications. The CVD diamond films are composed by grains with dimensions within 1–10 μm or 10–100 nm ranges, corresponding to the so-called microcrystalline diamond (MCD) and nanocrystalline diamond (NCD) varieties, respectively. Grain size strongly influences the CVD diamond surface roughness which in turn determines the tribological behavior of the coatings. In self-mated contacts, this gives rise to high initial friction (μ_{max}) levels, which is especially true for the MCD morphology ($0.35 \leq \mu_{\text{max}} \leq 0.65$ [1,2]). In this case, surface asperities have to fracture or to overcome each other during sliding, expending a large amount of mechanical energy, thus causing such high initial values of friction. After that, extremely low friction coefficient values are achieved in the steady-state regime ($0.02 \leq \mu_{\text{st}} \leq 0.05$ [1,2]) as well as a very low wear rate ($10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1} \leq k \leq 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ [1,2]), exhibiting excellent endurance.

Diamond-like carbon (DLC) films are amorphous carbon coatings presenting a mixture of sp^2 and sp^3 hybridizations. In fact, there are different forms of DLC whose structure, properties and tribological behavior depend on their sp^2 and sp^3 -bond character as well as of hydrogen content [3]. Generally, due to its low shear strength, when applied on a sliding surface, the DLC coatings can lower friction and wear and for that reason are considered as solid lubricants [4]. However, in abrasive conditions, DLC coatings do not have enough endurance [5].

The combination of DLC and CVD diamond in a bilayer coating gathers the best properties of the two films individually. This approach was reported by some authors [5–8] having different purposes. Csorbai et al. [6] prepared a pinhole-free thin DLC-diamond double layer for corrosion protection and assessed the effect of deposition parameters on the protective properties of the layers. Hanyu et al. [5] combined DLC with a CVD smooth surface diamond coating in order to improve the cutting performance of tools for the machining of aluminum alloys. The bilayer lead to a better anti-sticking property of cutting tools and successfully increased the tool endurance. Miyoshi [7,8] focused its study on tribological applications in ultrahigh vacuum, where CVD diamond presents a high coefficient of friction and low wear resistance. The deposition of a thin film of amorphous carbon on CVD diamond in one of the sliding parts decreased the coefficient of friction and the wear rate, proving to be an effective wear-resistant film, lubricating the diamond coating in ultrahigh

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vacuum [7]. In a previous work by the same author, tribological tests performed in dry nitrogen and in humid air revealed a low steady-state coefficient of friction and low wear rate, showing that the bilayer presents an excellent tribological behavior regardless of the environment [8].

The work hereby presented attempts to understand why an external solid lubricant DLC layer helps on increasing the total load that a CVD diamond coating can withstand before failure (load bearing capacity). The effect of dynamic friction is to add a compressive stress to the front edge of the moving contact and to intensify the tensile stress at the back edge [9]. As a result, yielding occurs at lower loads for the coatings presenting higher initial friction levels [9]. In the present work, the tribological performance of the DLC-diamond bilayers is tested using the self-mated reciprocating ball-on-plate configuration. Thin DLC films, with and without hydrogen, were deposited on the top of both the MCD and NCD coating varieties. DC magnetron sputtering was the chosen technique for DLC deposition due to versatility and ability to produce hydrogenated coatings by reactive sputtering [3]. Works reporting a similar combination of DLC and diamond layers used pulsed laser deposition [6], rf plasma CVD [5] and ion beam [7,8] techniques.

2. Experimental

CVD diamond films were deposited on silicon nitride (Si_3N_4) ceramic plates and balls. Plates of 10 mm of diameter and 3 mm of thickness were homemade using a preparation routine described elsewhere [10], while Si_3N_4 commercial balls of 5 mm of diameter (Cerbec[®], CoorsTek) act as counter bodies in the sliding experiments. The Si_3N_4 plates were ground and polished with 15 μm diamond slurry, ultrasonic cleaned and then seeded, together with the balls, for 1 h in an ultrasonic suspension using 0.5–1 μm sized diamond powder in ethanol, followed by cleaning with ethanol for 5 min. After surface pre-treatment, two varieties of CVD diamond were grown by hot-filament CVD technique: microcrystalline (MCD) and nanocrystalline (NCD) films. The deposition parameters used are listed in Table 1.

Diamond-like-carbon (DLC) layers were deposited by PVD on the diamond coated plates and balls, using a DC magnetron sputtering system. The target was a 2-in. diameter pure graphite plate with 3 mm of thickness, located at 10 cm from the substrate holder. A residual pressure near 1×10^{-5} mbar was attained before deposition. The gas used was argon to produce non-hydrogenated carbon films (DLC) and a mixture of argon and methane to produce hydrogenated carbon films (DLC-H), Table 1. The target was pre-sputtered for about 10 min before deposition, to remove any surface impurities, with the substrates temporarily protected by a shield. Silicon (Si) wafers were also coated with DLC and DLC-H, in order to assess film thickness by ellipsometry measurements (Jobin Yvon AutoSE ellipsometer, 70° incidence angle, 440–850 nm). The use of Si as a substrate makes easier the

experimental curve fitting procedure required to estimate the coating thickness by this technique.

All the coated substrates were characterized by atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa), field-emission scanning electron microscopy (Hitachi SU-70 FE-SEM) and μ -Raman spectrometry (Horiba Jobin Yvon HR800 at 325 nm). The tribological characterization of the DLC/diamond bilayers was achieved using a ball-on-flat reciprocating tribometer (PLINT TE67/R). Unlubricated self-mated tests were performed in ambient atmosphere (RH of 50–60%) at room temperature, with constant stroke (8 mm) and frequency (1 Hz). The duration of the tribological test was 2 h, which corresponded to a sliding distance of approximately 115 m. The normal applied load varied in the range 5–80 N (at intervals of 10 N, for loads > 10 N) applied directly over the ball specimens. For all samples, the critical load was determined by performing tests with successively higher loads until failure occurs. The friction force was measured by a load cell. Afterwards, all the samples were observed by SEM, AFM and μ -Raman spectroscopy. The wear coefficient of the balls was assessed by measuring the corresponding wear scar diameter in SEM [1], while AFM bearing function enabled volume loss quantification of plate wear tracks [11].

3. Results and discussion

3.1. Characterization of the diamond monolayers and the DLC/diamond bilayers

SEM top-view micrographs of the coatings studied in the present work are shown in Fig. 1. As it can be seen, the micro-sized grains (0.5–2 μm) of the diamond film (Fig. 1a) are still visible after coating with DLC and DLC-H (Fig. 1b and c). The main morphological difference between DLC/MCD bilayers and the MCD monolayer is the smoothing of the diamond grain edges by coating with the amorphous carbon film, as depicted in the insets of Fig. 1a–c. Samples coated with NCD present the distinctive nano-sized grain morphology even after being coated with amorphous carbon films, Fig. 1d–f. AFM scans performed in tapping mode assessed the surface roughness (RMS) of the unworn coatings (Fig. 2). No significant differences were found on samples before and after coating with DLC films confirming the results from SEM characterization. It is also clear, from these AFM data, that NCD coatings are much smoother than the MCD ones.

Cross-section views by SEM (an example is shown in Fig. 3) allowed the measurement of diamond film thicknesses of about 6 μm for MCD and 3 μm for NCD layers. DLC thicknesses estimated by ellipsometry measurements were found to be approximately 540 nm and 350 nm for DLC and DLC-H, respectively. The growth rate of DLC-H is lower than DLC because the deposition of hydrogenated amorphous carbon films is a reactive process that requires the addition of a hydrocarbon gas source, which reduces

Table 1
Conditions of deposition of diamond and DLC films.

| HFCVD | CH_4/H_2 | Ar/H_2 | Gas flow (ml min^{-1}) | Pressure (mbar) | Filament temperature ($^\circ\text{C}$) | Substrate temperature ($^\circ\text{C}$) | Deposition time (h) |
|-------|--------------------------|------------------------|--------------------------------------|----------------------|--|---|------------------------|
| MCD | 0.02 | – | 100 | 175 | 2300 | 800 | 6 |
| NCD | 0.04 | 0.1 | 200 | 100 | 2250 | 700 | 10 |
| PVD | Ar (sccm) | CH_4 (sccm) | Power (w) | Pressure (mbar) | Distance Target/ samples (cm) | Substrate temperature ($^\circ\text{C}$) | Deposition time (h) |
| DLC | 10 | – | 110 | 1.9×10^{-3} | 10 | 100 | 4 |
| DLC-H | 9.3 | 0.7 | 110 | 1.9×10^{-3} | 10 | 100 | 4 |

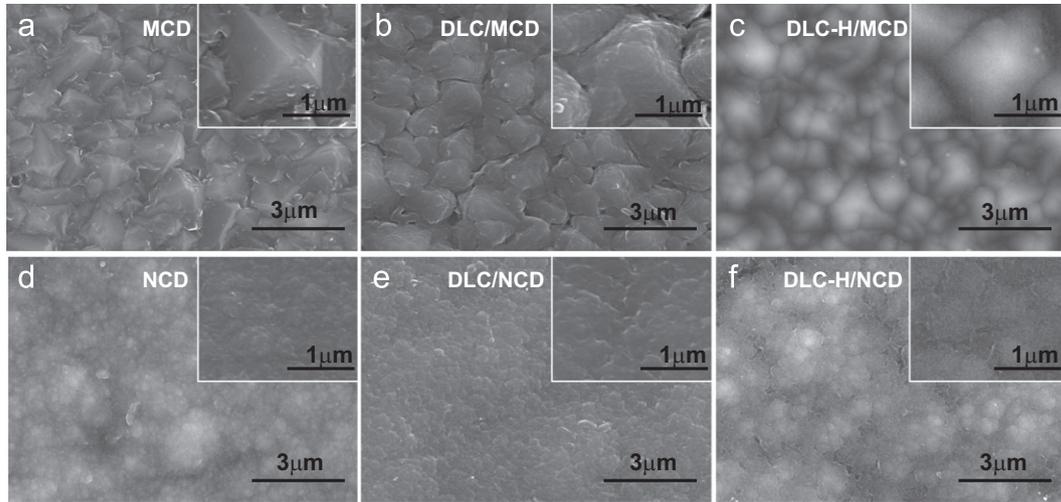


Fig. 1. Scanning electron microscopy (SEM) top-view micrographs of diamond coatings and DLC/diamond double layers. High magnifications are shown in the insets.

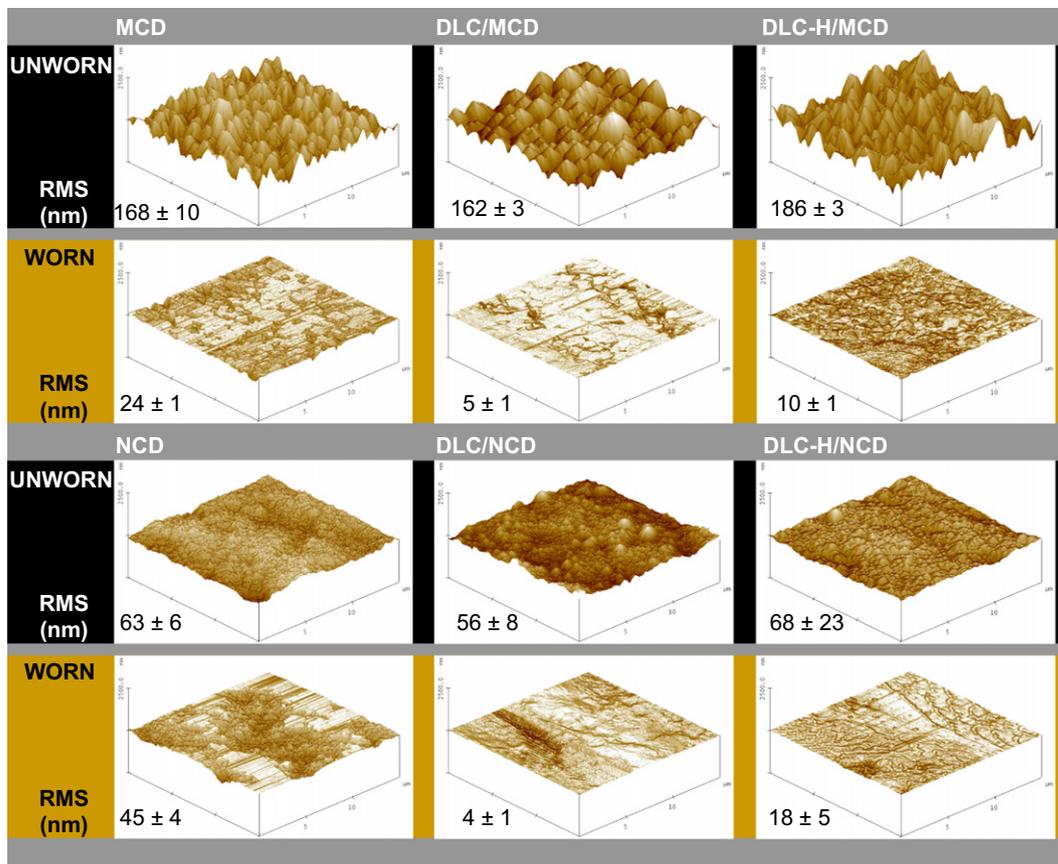


Fig. 2. Atomic force microscopy (AFM) scans of unworn and worn coatings and respective surface roughness values (RMS).

the partial argon pressure and decreases the sputtering rate of the carbon target [12]. Nonetheless, both amorphous carbon films are thin when compared to the diamond ones (6–18% of diamond thickness values) and for that reason unable to induce large morphological differences on diamond surface, as was shown by SEM and AFM analysis.

Raman spectra revealed the MCD and NCD signatures for the samples coated only with diamond, Fig. 4a and b. For the MCD layer, the main diamond peak (1331 cm^{-1}) is visible as well as the D and G graphitic bands (1365 cm^{-1} and 1565 cm^{-1} , respectively). For NCD,

the D and the G bands are wider and more intense than the diamond peak and there is an evidence of a new peak at 1170 cm^{-1} (C–H chains). After coating with DLC and DLC-H, those signatures are no longer detectable and a typical amorphous carbon spectrum arises instead. This is expected to happen as the 325 nm laser penetration depth is about 10–15 nm [13], lower than DLC thickness. Both DLC coatings present two bands: D and G. The D band appears at 1365 cm^{-1} and the G band is located at 1575 cm^{-1} for the non-hydrogenated film and at 1582 cm^{-1} for the hydrogenated one. The shift of the G band towards 1575 cm^{-1} indicates a slightly change on

carbon-bonding configuration of the film caused by hydrogen incorporation [14].

3.2. Friction coefficient and wear

The friction curves shown in Fig. 5 for the different tested samples were obtained under the maximum testing load that the films could withstand without failure (W_c , critical load). All the curves are characterized by an initial friction peak (μ_{max}), a running-in step that lasts for a short distance (< 10 m) in most of the cases, and a stage where the coefficient of friction levels off and tends to stabilise in low steady-state values (μ_{st}). The complete set of friction coefficient values is given in Fig. 6. The samples coated with MCD present higher initial friction peaks than the ones coated with NCD. This behaviour is related to the mechanical interlocking between asperities taking place during the relative motion of contacting surfaces [1], which is more operative in the case of MCD due to its higher nominal surface roughness (RMS), Fig. 2.

The DLC deposition on top of the diamond layer decreases the μ_{max} values, mainly in the case of the MCD coatings, Fig. 6. This lubricant effect is preminent for the combination DLC-H/MCD, reducing in 46% the value of μ_{max} but, above all, increasing the critical load (W_c) from 20 to 60 N, Fig. 5. The μ_{max} decrease observed for the DLC-H/MCD coated material is not the result of the higher applied load (60 N) since tests performed at 20 N also showed a lower value ($\mu_{max}=0.50$) than the one found for MCD ($\mu_{max}=0.76$). Instead, the structure and chemical bonds of DLC-H films are proposed as accountable for this behaviour. Several authors [15–18] reported that hydrogen on the DLC film surface is

responsible for a large decrease in the unsaturated carbon bonds at the interface when compared to non-hydrogenated films. Passivation of dangling bonds by the linking of H to C atoms reduces the attractive forces between the two surfaces in sliding contact and reduces friction [18]. Molecular dynamic simulations have supported the passivation hypothesis as an explanation for the low DLC-H friction [15,18].

Among the set of tested samples, DLC/NCD is the coating that presents worse frictional behavior. It has the longest running-in period and the highest steady-state friction coefficient, Figs. 5e and 6. SEM images of the wear track produced at the test load of 5 N, Fig. 7, reveal partial delamination of the film. This set of facts is an outcome of the contact between ultra smooth surfaces (RMS= 4 ± 1 nm, Fig. 2) and strong adhesion forces established among them, resulting from linkages with dangling bonds on the counterpart surface.

The wear coefficient values (K) depicted in Fig. 8 were assessed for plates and balls in accordance with Archard's law: $K=V/xW$, were V is the volumetric wear, x is the sliding distance, and W is the applied load. The coated plates present higher wear coefficients than the balls. This difference was expected and is a result of fatigue wear mechanism characteristic of intermittent loading on the flat specimen.

The NCD single layer exhibits the lowest assessed wear rate, with extremely low values ($3 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$), given that is one of the smoothest films and harder than DLC. As expected, the sample presenting the highest wear rate ($5.2 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) is the one which has the worst frictional behavior above described, the DLC/NCD bilayer.

In general, double layer coatings presented higher wear rates than the single ones, which does not surprises considering that the diamond film is covered with the amorphous carbon that is less hard, decreasing the hardness of the top ultimate layer, thus becoming more wear susceptible. Analysis of the wear track of DLC-H/MCD and DLC-H/NCD by Raman spectroscopy, Fig. 9, showed only MCD and NCD characteristic features attesting the removal of the softer layer during sliding. Nevertheless, the wear coefficient values assessed for double coatings are in the range of mild wear regime ($10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$).

Among the tested DLC coatings, hydrogenated amorphous carbon films are the ones presenting the lowest wear rates. In fact, in the literature, those films are described as being more wear resistant due to features such as self-healing ability, strain tolerance and compressibility which make them ideal solid lubricants [16].

3.3. Importance of the reduction of the running-in friction on the bearing capacity

In the present work there is one result that outstands: the reduction of the friction coefficient and the increase of the critical

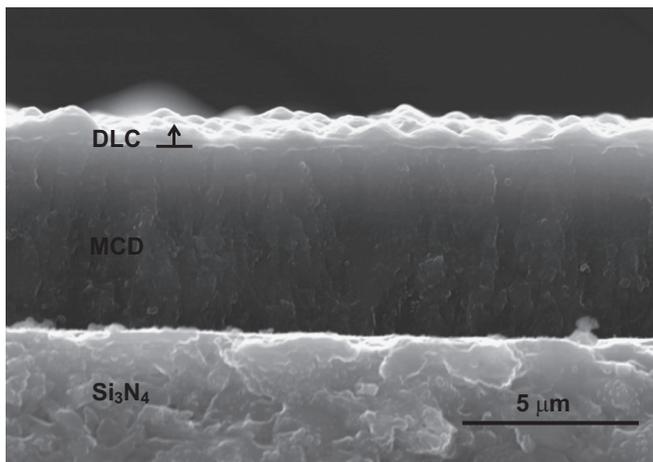


Fig. 3. Scanning electron microscopy (SEM) cross-section image of DLC/MCD bilayer coating on silicon nitride (Si_3N_4) substrate.

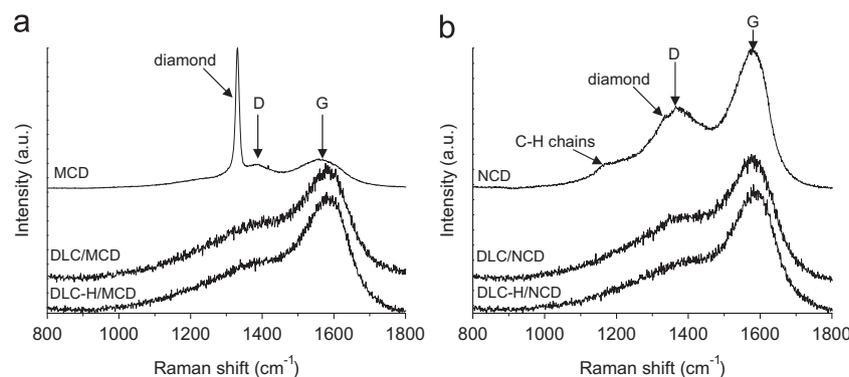


Fig. 4. UV micro-Raman spectra of as-deposited diamond coatings and DLC/diamond double layers: (a) MCD and (b) NCD as first layers, respectively.

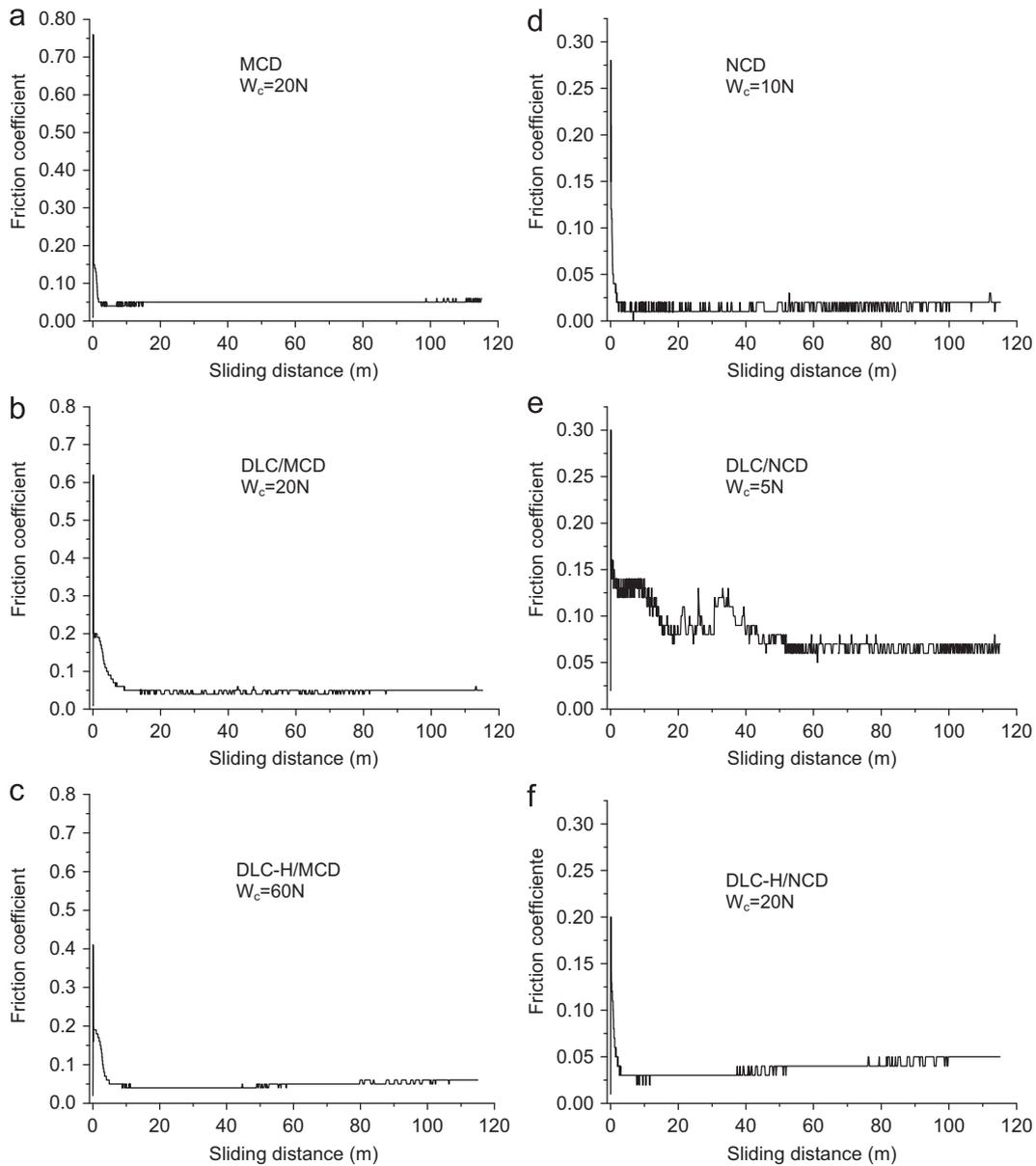


Fig. 5. Friction curve evolution as a function of sliding distance under critical load, for diamond coatings and DLC/diamond double layers.

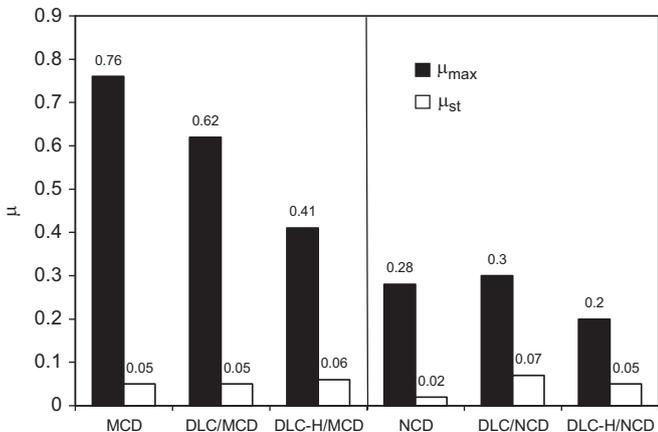


Fig. 6. Coefficient of friction of the homologous pairs under critical load: initial (μ_{max}) and steady-state (μ_{st}) values.

load when a thin coating of DLC-H is deposited on top of a MCD film. In this subsection, explanations based on contact mechanics will be discussed.

A first, simple, calculation demonstrates why the amorphous carbon films decrease the friction coefficient relatively to the uncoated MCD. This is related to the intrinsic elastic properties of the coatings, namely Young's modulus and Poisson's ratio and their effect in the maximum shear stress values (τ_1). Fig. 10 presents the τ_1 values resulting from the normal Hertzian contact of a spherical indenter on a flat surface, plotted as a function of z (distance to the surface). Calculation of τ_1 is made accordingly to the following equations [19]:

$$a = (3WR/4E^*)^{1/3} \quad (1)$$

$$p_0 = (6WE^*/R^2\pi^3)^{1/3} \quad (2)$$

$$\sigma_{xx} = \sigma_{yy} = -p_0[(1+\nu)(1-z/a \arctan(a/z)) - 0.5(1+z^2/a^2)^{-1}] \quad (3)$$

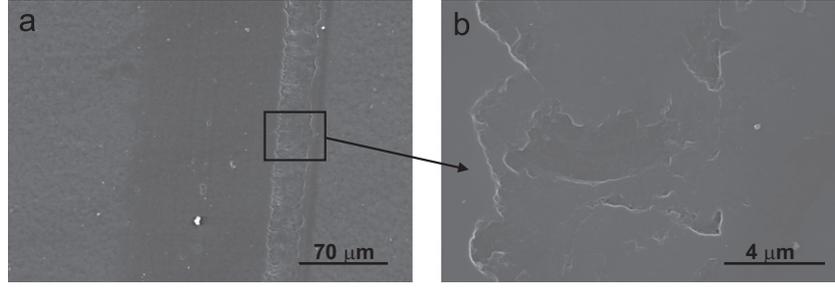


Fig. 7. Aspect of the wear track for sample DLC/NCD under an applied load of 5 N: (a) low magnification and (b) detail depicting the delaminated zone at the DLC/diamond interface.

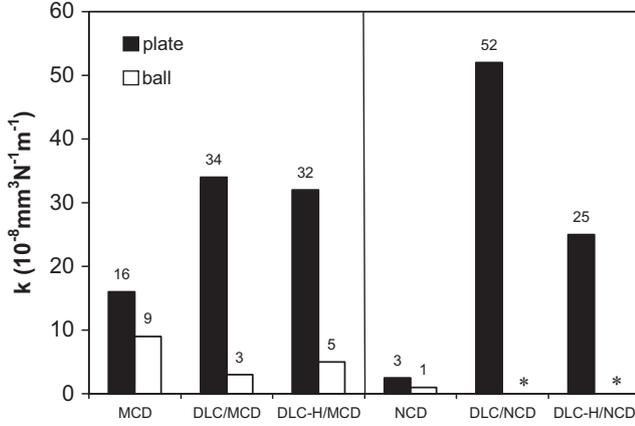


Fig. 8. Wear coefficient values for ball and plate specimens under critical load. * omitted value due to film failure.

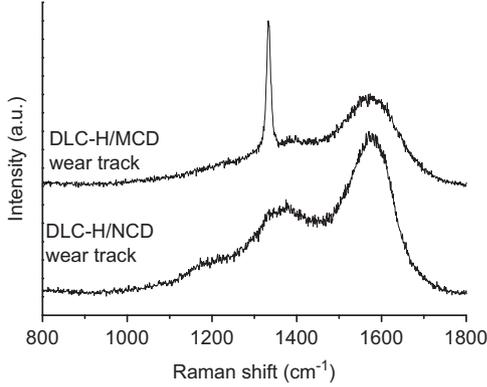


Fig. 9. UV micro-Raman spectra of worn DLC-H/diamond double layers.

$$\sigma_{zz} = -p_0(1+z^2/a^2)^{-1} \quad (4)$$

$$\tau_1 = 0.5|\sigma_{zz} - \sigma_{xx}| \quad (5)$$

where W is the normal applied force, R is the radius of the spherical indenter, a is the contact radius, p_0 is the maximum pressure, σ_{xx} and σ_{zz} are the normal stresses in the x and z -directions, and E^* is the composite modulus of the two surfaces given as $1/E^* = (1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2$ where E_i are the elastic moduli and ν_i are Poisson's ratios of the two contacting surfaces [19]. Literature values of the elastic constants were considered to be a realistic approximation: $E = 1143$ GPa and $\nu = 0.07$ for microcrystalline diamond [20], and $E = 87$ GPa and $\nu = 0.22$ for hydrogenated DLC coatings [21].

To calculate the curves shown in Fig. 10 homologous contacts (MCD/MCD and DLC/DLC) and an applied load of $W = 20$ N were

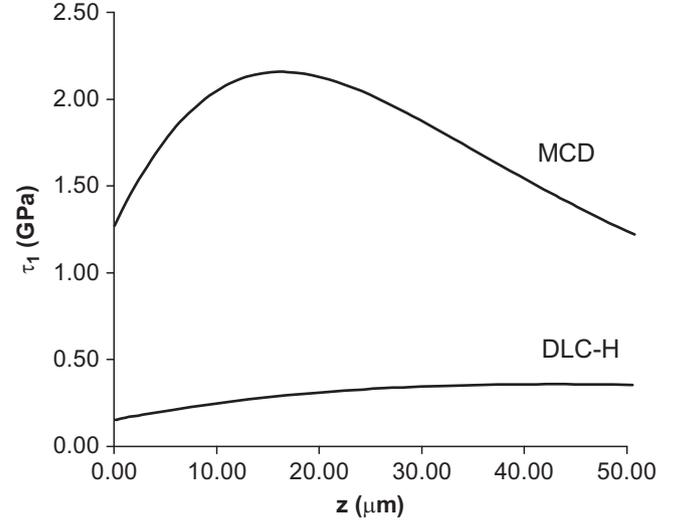


Fig. 10. Maximum shear stress evolution beneath the normal contact of a spherical indenter and a flat surface, both coated with MCD or DLC, for an applied load of 20 N.

used, as an example to illustrate the differences between these materials regarding the shear stress along the z -axis. It can be seen that DLC presents much lower maximum shear stress values than MCD, revealing a high potential to provide good lubricity when deposited on diamond coatings. This was proved in the present work, with the decrease of the coefficient of friction of MCD coatings during the first instants of sliding by the deposition of DLC thin films (Fig. 6).

The other significant result obtained is the increase of the critical load from 20 N, for homologous contacts of MCD, to 60 N, for homologous contacts of DLC-H/MCD (Fig. 5). Such improvement on the bearing capacity of the coatings is related to the net change of the stress field beneath the spherical contact provoked by friction, relatively to the static Hertzian contact [9]. In normal contact ($\mu = 0$), the maximum shear stress occurs below the surface, as it can be seen in Fig. 10. According to Hamilton [9], friction moves this original maximum closer to the surface and, most important of all, a new region of likely failure develops in the surface at the back edge of contact ($x = -a$). Beyond $\mu = 0.25$ this new region dominates the stress field, i.e. the point of failure is located at the surface. As it is a three-dimensional stress field, the von Mises yield parameter, $\sqrt{J_2}$, is used to describe it. The values of the maximum yield parameter are given by [9]:

$$\frac{\sqrt{J_2}}{p_0} = \frac{1}{\sqrt{3}} \left\{ \frac{(1-2\nu)^2}{3} + \frac{(1-2\nu)(2-\nu)\mu\pi}{4} + \frac{(16-4\nu+7\nu^2)\mu^2\pi^2}{64} \right\}^{1/2} \quad (6)$$

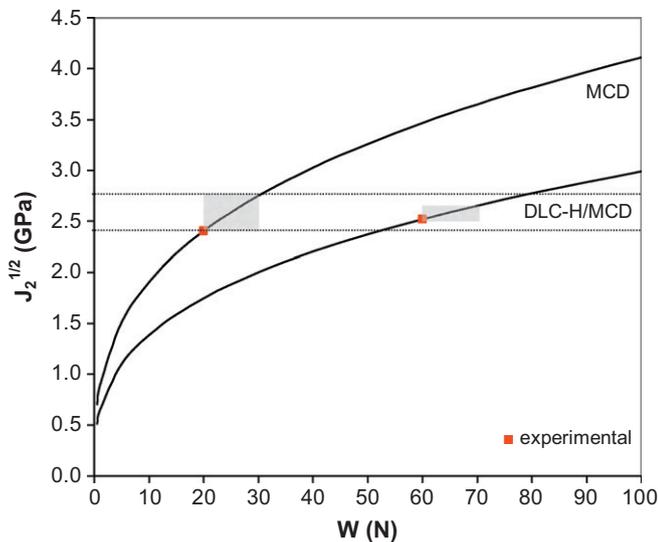


Fig. 11. Maximum von Mises yield parameter as a function of applied load for homologous sliding contact of MCD and DLC-H/MCD coated balls and plates. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

This equation was used to plot $\sqrt{J_2}$ as a function of normal load (Fig. 11) for the MCD monolayer and the DLC-H/MCD double layer homologous tests. In these, the initial coefficient of friction is always higher than 0.25 (Fig. 6) and the failure of the coating is likely to start at the surface induced by a critical load value. The coefficient of friction used in the calculations is the average value assessed during the tribological tests for each coating, since friction showed to be almost independent of applied load (standard deviation was only 0.06). Here, in the calculation of p_0 , due to the very small thickness of the MCD and DLC-H/MCD coatings, and for a more realistic approach, the elastic deformation was calculated using only the contribution of the ceramic substrates, while for the XY surface deformation Poisson's ratio used is that of the diamond.

In Fig. 11, the little red square marks indicate the test load, immediately below the one where failure occurred or, as it has been named, the critical load. However, the tests were performed with intervals of 10 N, so there is a window of load values, the big gray square, that were not tested and that the coatings may still bear. The von Mises yield parameter has a range of possible values in that window, defining the stress range that the coatings may be able to withstand. From the analysis of the curves of Fig. 11, it can be concluded that the reduction of the μ value for the DLC-H/MCD double layer results in an increase of the critical load when submitted to the same stress state $\sqrt{J_2}$ of MCD. The experimental value obtained for the critical load of DLC-H/MCD (60 N) is within the interval of predicted values (52–80 N) determined from the range of maximum yield parameter values of MCD (limited by the horizontal dotted lines in Fig. 11).

The graph of Fig. 11 is very clear in showing the importance of reducing the friction coefficient to improve the load bearing capacity of the coatings. The approach hereby discussed can be applied to other combinations of films and contribute to the design of low-friction and high-bearing capacity systems for high-demanding tribological applications.

4. Conclusions

DLC/diamond bilayers were successfully produced by growing thin (350–540 nm of thickness) DLC lubricant coatings, using DC

magnetron sputtering, on the top of CVD diamond films produced by HFCVD (thickness range: 3–6 μm). Two grain-size diamond varieties, microcrystalline (MCD) and nanocrystalline diamond (NCD), were combined with two types of DLC films, non-hydrogenated and hydrogenated ones (DLC-H). No significant morphological differences were induced on the diamond surfaces by the deposition of the DLC outer layer. However, UV-Raman spectroscopy revealed a typical amorphous carbon spectrum instead of the diamond signature.

Unlubricated self-mated tests assessed the tribological behaviour of the coatings. Samples coated with MCD present higher initial friction peaks than the ones with NCD due to the higher nominal surface roughness. The deposition of DLC films allowed the reduction of friction values in the first instants of sliding, mainly in the MCD case. The DLC outer layers perform a sacrificial role in such initial moments as they rapidly worn-out. Notably, a significant increasing of the critical load for film failure, from 20 N to 60 N, takes place due to the decrease of the initial friction peak, from 0.76 to 0.41, when a DLC-H/MCD double layer is used. While the elastic properties of DLC-H accounts for a reduction of the shear stress in a static hertzian contact, the application of the von Mises maximum yield parameter criterion to sliding contacts demonstrates to be an adequate method to describe the dependence of the bearing capacity on the initial friction coefficient value.

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