

Energy Filtering Transmission Electron Microscopy and Atomistic Simulations of Tribo-induced Hybridization Change of Nanocrystalline Diamond Coating

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Abstract

The tribofilm formed on nanocrystalline diamond coating during ultralow friction in presence of water and glycerol lubrication has been studied experimentally by energy filtering transmission electron microscopy (EF-TEM) and electron energy loss spectroscopy (EELS) on focus ion beam (FIB) cross sections. Surprisingly, even under mild tribological conditions, a tribo-induced hybridization change (sp^3 towards sp^2) can be clearly detected at the top of the coating resulting in the formation of a 40 nm thick amorphous sp^2 rich carbon layer with embedded diamond nanoparticles less than 5 nm diameter. Classical molecular dynamics simulations of diamond single crystal asperity collisions can explain this finding. Tribochemical amorphization of the contact zone between the colliding diamond grains followed by fracture events at the asperity shoulders produces ultra-nanodiamonds that remain attached to the amorphous carbon phase. An additional atomistic sliding simulation

of two ultra-nanocrystalline diamond coatings yields an amorphous sp^2 rich carbon layer that grows at a rate that is comparable to corresponding layers on the softest diamond single crystal surfaces.

1. Introduction

Nanocrystalline Diamond (NCD) is one of the most promising coating materials due to its excellent resistance to abrasion associated with ultralow friction in various environments. Superhard and ultra-smooth carbon films, like tetrahedral amorphous carbon (ta-C) and NCD, lubricated with environmental friendly molecules provide more sustainable solutions compared to today's existing coatings and traditional lubricants. Indeed, previous studies have demonstrated that superlubricity could be reached with OH-containing organic compounds as lubricants (such as carbohydrates, polyols esters, fatty acids and water¹⁻⁵). This amazing friction behaviour is commonly associated with changes of the hybridization of carbon atoms from sp^3 to sp^2 states⁶⁻⁸ and with the swift saturation of dangling bonds (generated during sliding at the exposed surface) by hydrogen and oxygen from the environment.⁹⁻¹¹ Recently, based on combined experimental and first-principles analyses, friction results with NCD coatings lubricated by H_2 or H_2O have confirmed the major role of dangling-bond passivation by H and/or OH species to generate low and ultralow friction.¹² Nevertheless, strong structural transformations of the bulk of the diamond coating under friction cannot be excluded. Previous studies using TEM imaging coupled with electron energy loss spectroscopy (EELS) have evidenced major structural changes for hard amorphous ta-C films, consisting in a clear carbon hybridization change from sp^3 to sp^2 , after ultralow friction in the presence of glycerol.¹³ The low-density sp^2 rich amorphous phase is a manifestation of a tribochemically transformed phase of matter that is found at the sliding interface in many triboystems.¹⁴

Even for single crystal diamond a tribo-induced phase transformation (TPT) yielding a sp^2 hybridised amorphous layer has been found in classical molecular dynamics (MD) simulations¹⁵. This finding has been subsequently confirmed by TEM/EELS measurements of coarse-grained diamond coatings after high wear ring-on-ring tribological testing¹⁶. Another study combining X-ray absorption near-edge fine structure (XANES) and MD also observed the formation of a soft amorphous carbon (a-C) layer with increased sp^2 content on ta-C and

on ultra-nanocrystalline diamond (UNCD)¹⁷. This soft amorphous sp^2 -carbon rich layer was found to grow faster on the amorphous ta-C material than on the UNCD material under the same sliding conditions.¹⁷ A recent atomistic study¹⁸ reports that the sliding of H-passivated ta-C asperities under extreme tribological conditions results in sp^2 rich interface layers. The authors found that even lubrication with a monolayer of hexadecane didn't prevent the TPT although the thickness of these a-C layers was drastically reduced in the lubricated case. All these studies provide strong support to the conjecture that the formation of an a-C tribofilm material is a rather universal mechanism governing the running in and wear of carbon hard coatings. It remains however unclear whether such a tribofilm also forms under low friction conditions with very mild wear.

The aim of this work is an accurate investigation of surface structural modification undergone by lubricated NCD coatings. In order to address the question if the a-C layer emerges even under ultralow friction conditions we performed energy-filtered TEM (EFTEM) imaging coupled with low-loss EELS. Special attention was paid to the plasmon-loss energy region corresponding to collective excitation ($\pi+\sigma$) valence electrons, as volume plasmon excitation. Plasmon EELS has already been investigated by Oleshko *et al.*¹⁹⁻²¹ to evaluate mechanical properties of different carbon materials in the TEM.

Although EFTEM experiments are able to detect a possible TPT, it is quite impossible to infer the underlying mechanism from microscopy results alone. Therefore, the origin of experimentally observed tribo-induced structural modification were studied also by classical MD employing a screened²² second generation reactive empirical bond order potential²³ (REBO2) – a methodology that had been successfully used in a previous publication to reveal the mechano-chemistry occurring during the sliding of flat single crystal diamond surfaces¹⁵.

In the current work we extend our scope and investigate the influence of roughness and polycrystallinity on TPT in diamond. The tribological behaviour of rough diamond surfaces was modelled on two scales. On the single asperity level, the collision of two diamond grains revealed the fundamental processes governing the topographical and structural evolution of the top surface region of asperities. On the polycrystalline level, the sliding of two UNCD tribo-pairs was performed in order to obtain deeper insights into the formation of the sp^2 -rich surface layer on the NCD under vacuum.

2. Ultralow friction of diamond coatings

Adherent and smooth nanocrystalline diamond coatings were deposited on titanium-based substrates by a Micro-Wave Plasma Activated Chemical Vapour Deposition (MW-PACVD) process at moderate temperature, lower than 600°C, from CH₄-CO₂ species.²⁴⁻²⁶ An accurate investigation of the surface and structure of the NCD coatings undertaken by EFTEM imaging coupled with low-loss EELS is presented in this work. The ultralow friction behaviour of the NCD coatings in the presence of water and glycerol OH-containing molecules has been studied using gas phase lubrication.

2.1 Characterisation of pristine NCD coatings

The properties of these NCD coatings (surface roughness, hardness, Young's modulus) are correlated to the MW-PACVD process through the concentrations of the gaseous precursors used in the plasma.²⁷⁻²⁹ For this study, a fairly good quality NCD coating was selected combining high sp³ content of about 94% and very low surface roughness of 35 nm in RMS (see table 1). The 100 nm-width fine columnar crystal structure of this NCD diamond coating is shown by the TEM image of a transverse cross-section nanomachined by Focus Ion Beam (FIB) technique [Fig. 1]. The 33 eV maximum energy of the plasmon peak recorded on this NCD coating clearly indicates a high sp³/sp² ratio close to pure diamond crystal [Fig. 2]. The hardness (H) can be estimated from the energy of the volume plasmon peak according to the empirical relationship (1) proposed by Howe and Oleshko.²¹ This relation is known to be quite accurate for hydrogen-free carbon materials.

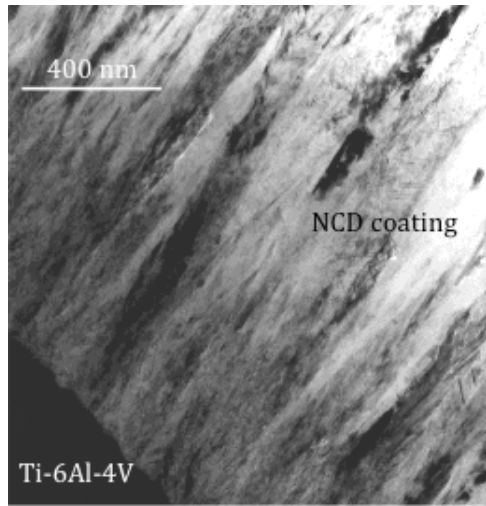
$$\log(H) = -7.44 + 6.1 \log(E_p) \quad (1)$$

Table 1, however, shows that the calculated hardness (66 GPa) is significantly smaller than the value obtained experimentally by nano-indentation (90 GPa). This can be attributed to the presence of defects between nanograins that favour plastic deformation process.

Table 1:

Details of diamond growth conditions ($P = 1.33$ kPa, $T = 600^\circ\text{C}$) and corresponding coating characteristics. Surface roughness was determined by AFM, diamond purity " $\text{Csp}^3/\text{Csp}^2$ " by Raman spectroscopy and EELS, hardness by nano-indentation, biaxial modulus by BLS, residual stresses by Raman spectroscopy and calculated thermal stresses. The values of H, D and R evaluated from the plasmon peak maximum energy were also reported.

Gaseous mixture	Surface roughness RMS (nm)	sp^3/sp^2 by Raman (%)	Calculated Hardness (1) (GPa)	Hardness by indentation (GPa)	E (GPa)	Thermal Stresses (GPa)
37,5% CH_4/CO_2	35	94	66.5	90	930	$-5,3 \pm 0,4$

**Figure 1 :**

TEM image of a 1350 nm thick NCD coating deposited on Ti-6Al-4V alloy substrate with a 37.5% $\text{CH}_4\text{-CO}_2$ mixture. A Pt protective layer was deposited on the NCD coating before ion machining to protect the carbon structure.

The presence of a 5-15 nm thick sp^2 -rich layer at the top surface of the NCD pristine coating was clearly revealed by energy-filtered imaging recorded at 6 eV energy-loss. This energy corresponds to the transition π/π^* in graphitic carbon [see inset in Fig. 2]. This layer seems to be formed during the last steps of the deposition process when the microwave plasma is suddenly stopped. The presence of this thin sp^2 -carbon rich layer at the top surface of the carbon coatings has already been observed for other hard DLC coatings, like ta-C.³⁰

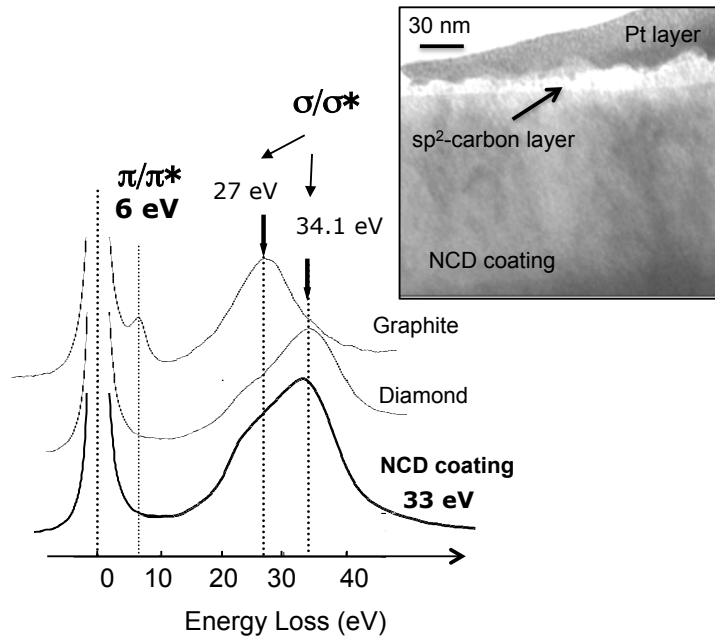


Figure 2 :

Comparison between the EELS spectrum recorded on the FIB cross-section of the NCD coating and the spectra of graphite HOPG and diamond standard materials. An energy-filtered image recorded at 6 eV is shown in the inset of the figure. A sp^2 -carbon- rich layer of about 5-15 nm thick (depending on the area) can be observed at the extreme surface (just below the protective Pt layer deposited on the NCD coating before nanomachining).

2.2 Gas phase lubrication of NCD coatings

Friction experiments were performed in gas phase environment using a dedicated environmental controlled analytical tribometer named ECAT³¹. The diamond-on-diamond friction experiments were carried out with a reciprocating pin-on-flat tribometer situated in an UHV chamber in the presence of pure glycerol or water vapour pressures. Prior to sliding tests, samples were cleaned with heptane and alcohol ultrasonic baths and then introduced into the UHV chamber where they were heated at 150°C to eliminate contamination (mainly hydrocarbon and water). The gas pressure was adjusted to 1 mbar for both glycerol and water vapours. Once the desired gas pressure was attained in the UHV chamber, the stationary hemispherical pin was loaded against the flat by a normal force of 3 N generating a contact pressure of about 300 MPa and the sliding speed was fixed at 0.001 m/s. Such load conditions in the gas phase drives the system into the severe boundary lubrication regime. The friction coefficient of NCD/NCD friction pair under ultra-high vacuum (UHV) suddenly increases to high value, of about 0.7, after a transient period corresponding to a few sliding cycles. This regime is thought to correspond to the removal of hydrogen from the carbon surface [Fig. 3(a)]. Consequently, a dark wear track on the surface of NCD coated-flat is

visible optically [Fig. 3(b)] in good agreement with previous results obtained with diamond material³². It is qualitatively explained by the breaking and formation of C-C bonds¹⁵ between the two surfaces containing dangling bonds. In comparison, the introduction of 1 mbar of glycerol or water, drastically decreases friction from 0.25 - 0.20 in the first 100 cycles until a very low level (below 0.05) is obtained. Moreover no significant wear is observed in such lubrication conditions [Fig. 3(b)]. ToF-SIMS surface analyses were carried out on diamond surface after friction experiments in similar conditions but using an isotope of water (heavy water D₂O). Results have clearly evidenced significant changes in surface chemistry of diamond after friction.¹² The amounts of D and OD ionic species, coming from the decomposition of D₂O molecules, were at least three times more abundant inside the sliding track than outside. This result clearly demonstrates the passivation of carbon dangling bonds generated at the sliding surfaces during friction by hydrogen and/or hydroxyl groups and this is the key factor to explain the ultralow friction.

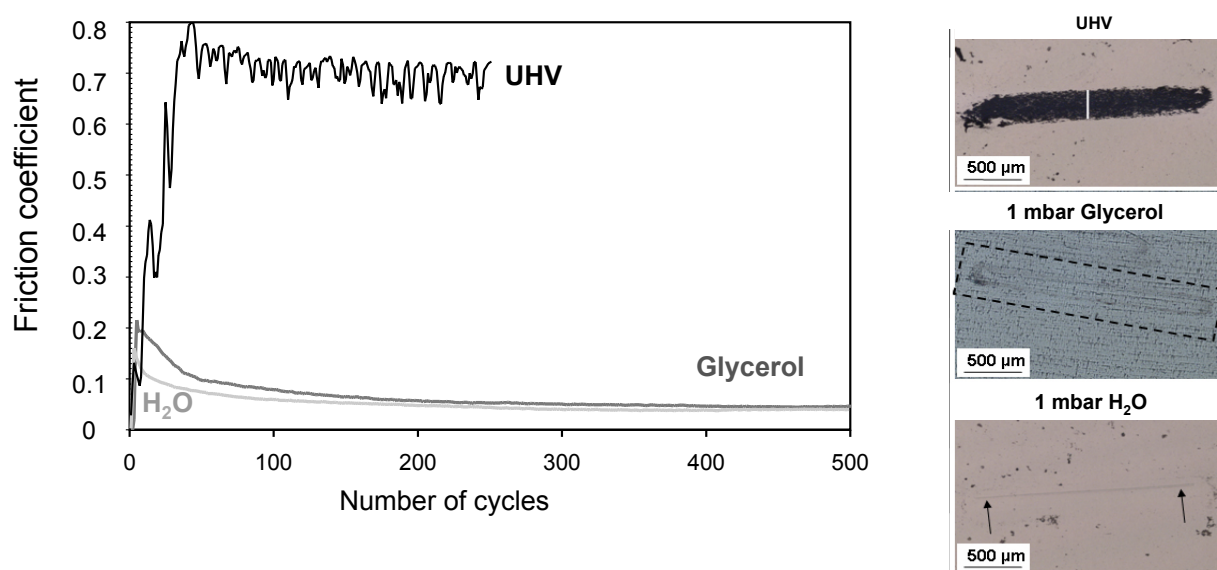


Figure 3:

- a) Friction coefficient vs. the number of passes for NCD/NCD friction pairs at 25°C in UHV (in black), with 1 mbar of glycerol vapour pressure (in dark grey) and in 1 mbar of H₂O vapor (in light grey);
- b) Optical images of the corresponding wear tracks formed during friction experiments presented in Fig.3a).

3. Experimental evidence of friction-induced hybridization change of diamond

The structural modification at the surface and in the bulk of NCD coating after low friction experiment was investigated by EFTEM with electron spectroscopic imaging (ESI) method

on a FIB cross-section nano-machined accurately inside the wear track. HRTEM observations coupled with electronic diffraction studies have been carried out to accurately identify the structural modifications.

3.1 FIB EFTEM analysis

EFTEM with electron spectroscopic imaging (ESI) method is able to produce elemental mapping from FIB prepared specimens as described by Lavergne *et al.*³³ A method of processing ESI images to improve the carbon K-edge spectra extracted from ESI images was developed by Yan *et al.*³⁴ The ESI image recorded at 6 eV energy-loss presented in figure 4 can be compared with the image performed on the pristine NCD coating [inset image in Fig. 2]. It can be seen that the thickness of the sp^2 -rich carbon layer at the top surface has increased from 10-15 nm to about 40 nm after the lubricated test. The sp^2 hybridization change of sliding diamond-like carbon surfaces under ultralow friction was also observed for amorphous ta-C coatings but with a larger thickness of 50 nm.³⁰

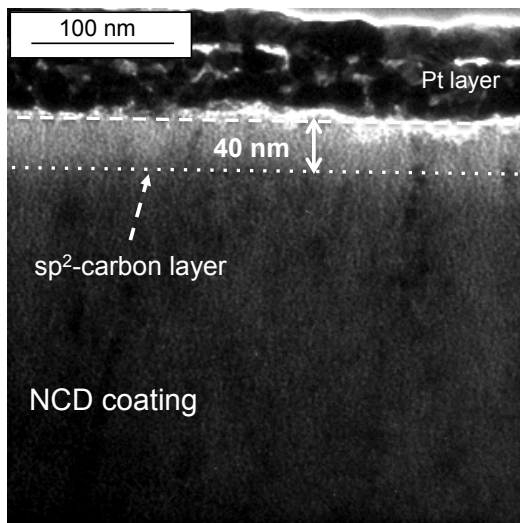


Figure 4:

Energy filtered image recorded at 6 eV on the rubbed NCD coating inside the friction track. A sp^2 carbon layer of about 40 nm thickness can be visualized at the extreme surface (just below the protective Pt layer).

The EFTEM in combination with the ESI method was also used to investigate the structure of the bulk of the NCD coating. A series of energy-loss images were acquired between 13 and 40 eV. The image obtained at 30 eV is presented in Figure 5. EELS low-loss spectra were

reconstructed retrospectively from six selected areas inside the coating, position 6 was the deepest inside the coating while the top surface corresponds to position 1.

The comparison of spectra obtained from positions 6 to 3 indicates that the main NCD coating remains homogeneous with high plasmon loss peak energy of 32.5 eV. However, a shift in the energy of the peak is clearly observed for the positions 1 and 2 at the top surface of the NCD coating, corresponding to a decrease of this energy. Table II summarizes the energies and the corresponding calculated hardness according to Eq. (1). This result clearly indicates a significant reduction in hardness at the top surface of the NCD coating well correlated with the hybridization change.

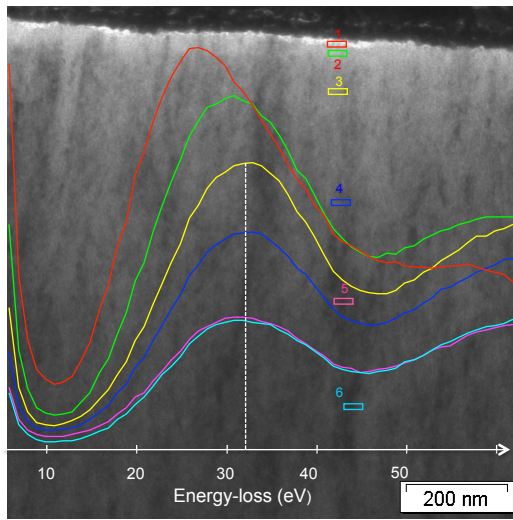


Figure 5:

Energy filtered image recorded at 30 eV inside the friction track for NCD coating with retrospective analysis spectra from a set of images between 13 and 40 eV. Spectra are obtained on six positions indicated in the picture (6-3 main coating and 1-2 top surface of coating).

Table 2:

Energy of low loss peak of the six spectra extracted from Fig. 5 and their corresponding calculated hardness from Eq. (1).

Position	E (eV)	H (GPa)
6-3	32,5	60.6
2	30	37.2
1	27	19.5

3. 2 HRTEM observations coupled with electron diffraction studies

To go further in the characterization of the modified top layer with increased sp^2 carbon content, an electron diffraction study was performed in this zone and corresponding zero-loss energy filtered annular dark field images were obtained on the selection of the (002) ring of graphite. The electron diffraction of the top surface of NCD coating [Fig. 6] shows a diffuse graphite ring corresponding to very small sp^2 carbon clusters. The surface layer is practically amorphous with no preferential orientation (continuous ring). This observation is in good agreement with the strong decrease of hardness evidenced by the shift in the energy of the plasmon loss peak maximum [Fig. 5]. HRTEM images performed on the corresponding top layer of NCD material show that some residual grains with a size below 5 nm, are embedded inside the amorphous sp^2 -carbon rich matrix [Fig. 7(a)] suggesting an attrition mechanism acting on the NCD during loading by pressure and shear. An optical diffraction study [Fig. 7(b)] performed on selected areas of the image shows the typical diffraction pattern of {111} diamond planes with a characteristic interplanar distance of $d_{\{111\}}=2.056 \text{ \AA}$. The presence of diamond nano-grains embedded inside the amorphous sp^2 -carbon rich matrix has been confirmed by other HRTEM images.

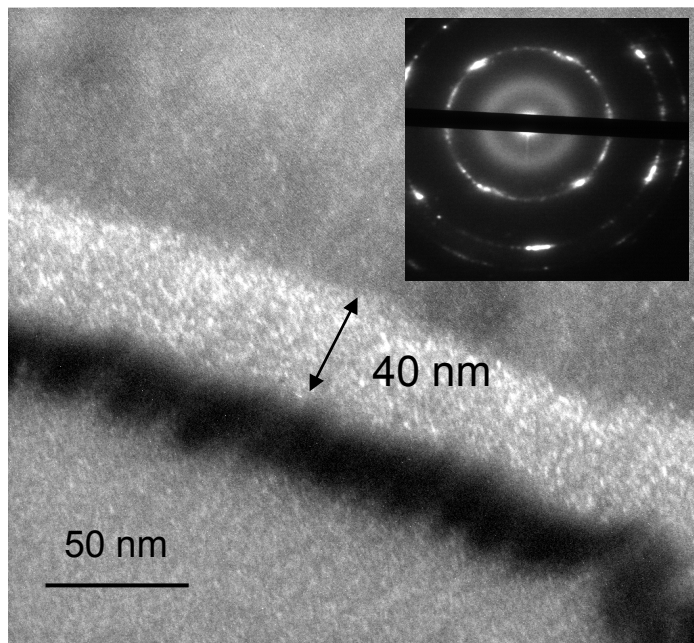


Figure 6:

Dark field image of the rubbed NCD coating performed with the aperture positioned on the (002) ring. This image shows an about sp^2 layer with short range graphitic order about 40 nm thick formed at the top surface of the NCD coating during the friction experiment.

[Fig. 8(a)] shows the interface between the NCD coating and the top layer in high resolution TEM. It is interesting to observe some ordered graphitic planes and even fullerene-like structures in addition to the “nanodiamonds”. The numerical diffractogram performed on this fullerene-like structure is consistent with the basal plane distance of (002) graphite layers. The measured inter-planar distance is about 0.369 nm, it is very close to the distance measured for carbon nano-onions synthesized by annealing diamond nanoparticles at 1700°C for 10 min studied by L. Joly-Pttuz et *al.*³⁵ This is about 10% more than the 0.336 value found for bulk graphite and can be related to the small size effect and the curvature of the graphitic layers in the nested structures. The total volume fraction of these graphitic structures is, however, significantly lower than for diamond nano-grains. We think that the sp² rich layer and the nano-crystallized structures embedded inside are mainly formed at the beginning early stage of the lubricated test when friction is relatively high (0.2-0.3). In the following, we focus on understanding the formation and destruction of nanodiamonds rather than graphitic structures in the molecular dynamics simulation described in the next section.

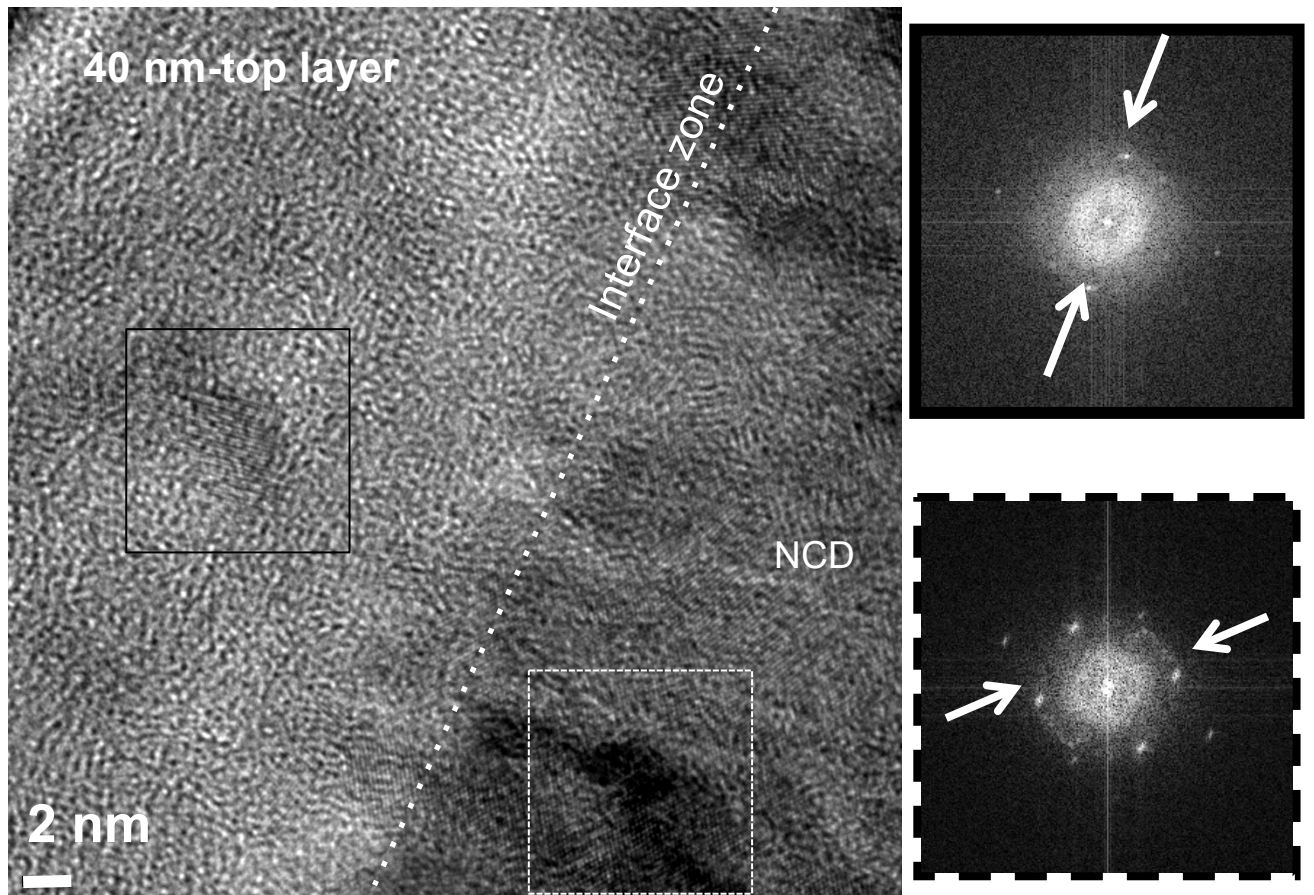


Figure 7:

- a)** HRTEM image performed on the FIB cross-section of rubbed NCD coating after ultralow friction. The 40 nm-thick amorphous layer with an increased sp^2 carbon content formed on the top of the NCD coating is clearly seen. Some residual diamond grains with a nanometric size, below 5 nm, can be observed inside the amorphous matrix rich in sp^2 -carbon (surrounded area in black).
- b)** Optical diffraction patterns of the diamond nanograin image seen inside the 40 nm-thick amorphous layer (surrounded area in black) and of a diamond grain inside the NCD coating (dashed white line).

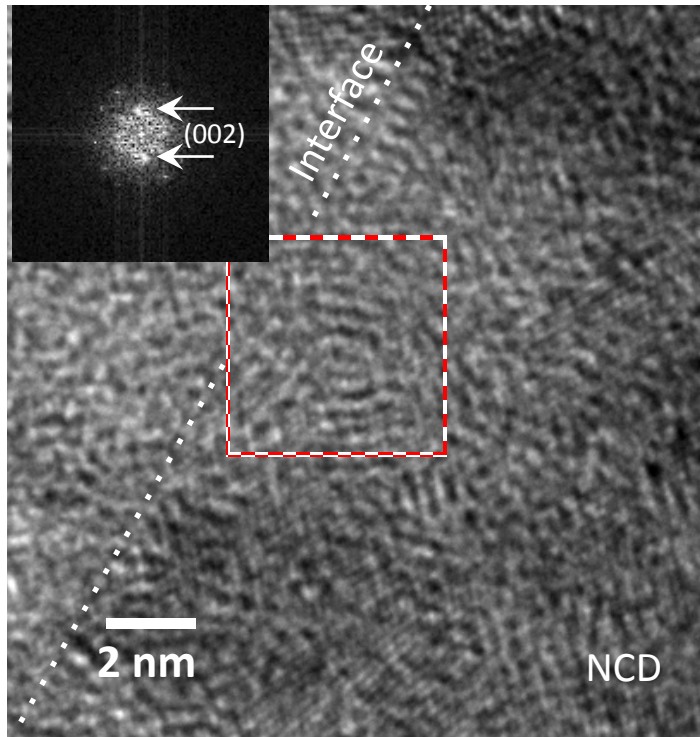


Figure 8:

HRTEM image of the interfacial zone between the NCD coating and the top 40 nm-thick amorphous layer showing the presence of some ordered graphitic planes and even a fullerene-like structure. The numerical diffractogram corresponding to the surrounded area shows special frequencies close to those of (002) graphite basal planes.

4. Evidence of rehybridization in NCD from atomistic modelling

Classical MD simulations of three different diamond tribosystems were performed in order to elucidate the mechanism underlying the formation of the observed sp^2 -rich a-C overlayers as well as the origin and stability of the interspersed diamond nanoparticles. Since

the initial NCD surface had a nanoscale roughness the collision of two diamond grains represents a generic tribological process step during the initial stage of sliding. Therefore, the collision of two diamond asperities was studied in our first simulation. The effect of polycrystallinity was addressed in a second simulation that considered two UNCD surface in sliding contact. In a third simulation, diamond nanoparticles in an amorphous carbon matrix under high shear strain was investigated in order to explain the experimentally observed stability of the diamond /a-C composite.

4.1 Numerical methods

In molecular dynamics simulations Newton's equations of motion are solved for a set of atoms controlled by appropriate boundary conditions. Ideally, the forces on the atoms should be derived from a solution of Schrödinger's equation for the valence electrons of the C atoms within the studied systems. However, since the tribological dynamics of two diamond surfaces usually involves thousands of atoms, such quantum derived forces are not feasible and classical force fields are used to propagate the systems over typical time scale of the order of nanoseconds. Here, we employed Brenner's classical Reactive Bond Order Potential in its revised version (REBOII) to derive a force field that is suitable for tribological simulations of carbon systems. The original short-ranged version of the REBOII potential fails in a faithful description of the fracture in diamond and the hybridization-density-relationship in amorphous carbons^{22,36} and therefore we made use of our version with added screening functions^{22,36} (scr-REBO II) that provide a reliable description of the forces for the breaking of bonds during tribological loading of the considered systems. While the simulation of the diamond asperity collisions and the shearing of a diamond/a-C composite were performed using the in-house code ATOMISTICA developed at the Fraunhofer IWM, the UNCD sliding calculations were conducted employing the LAMMPS software suite.

4.1.1 Setup of the diamond asperity collision

In our first simulation, two diamond asperities were constructed starting from 6.06x6.06x4.15 nm³ square base columns with face normals aligned along the diamond cubic directions. The final geometry was obtained by cutting the columns in order to expose 4 close packed (111) surfaces as show in Fig. 9a. The top parts of the asperities were terminated by (001) surface with a (2x1) reconstruction. Hydrogen atoms were then added to saturate the surface (white

spheres in Fig. 9a). This procedure resulted in a tribo-system consisting of roughly 40000 atoms (Fig. 9a).

In the lower (upper) asperity the bottommost (upmost) atoms in a 0.4 nm thick layer were treated as a rigid body (marked grey in Fig. 9a). Another 0.4 nm layer of atoms in the neighborhood of both rigid zones were thermalized to 300K during the whole simulation by Langevin dynamics³⁷ with a relaxation time constant of 1.5 ps (zones marked yellow in Fig. 9a). Contact of the asperities was achieved by displacing the block of rigid atoms in the top asperity at a constant velocity of 14.1 m/s in $[-110]$ direction (i.e. with an angle of 45° with respect to the $[010]$ -axis). The relative position of the two asperities was chosen such that the projected overlap h was 0.7 nm in $[001]$ direction (see Fig. 9a) during the whole simulation ensuring that the further dynamics resulted in an inelastic collision of the asperities.

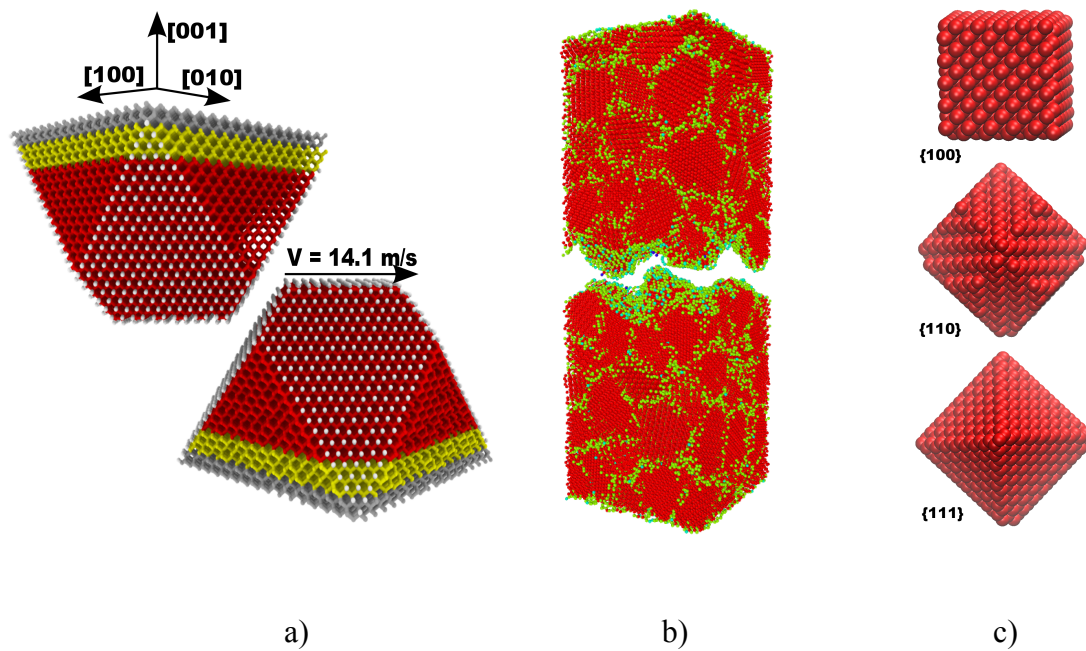


Figure 9:

Setup of the atomistic simulations.

- a) Single asperity collision: grey atoms are kept rigid, yellow atoms are thermalized to room temperature and red atoms are free to move. White atoms represent hydrogen.
- b) UNCD tribocouple: carbon atoms are colored according to their hybridization: red for sp^3 , green for sp^2 , cyan for sp^1 and blue for 1-fold coordination.
- c) Shear cell simulations of diamond particles in a-C matrix: configuration of the initial diamond crystallites before their embedding into the amorphous matrix.

During the simulation the coordination (hybridization) of every carbon atom was calculated, by counting the number of neighbors, inside a cutoff radius of 1.85 Å. Atomic stress tensors were computed from the atom-resolved virial in combination with a Voronoi tessellation to determine the atomic volume. The local Green-Lagrangian strain was determined by searching the deformation gradient tensor that best maps atomic position between a local reference configuration and the current local configuration³⁸ within a radius of 3 Å.

4.1.2 Setup of UNCD sliding simulation

Two UNCD samples were constructed by a Voronoi method. This yielded two tribopartners consisting of 83 grains each with an average grain size around 2-3 nm. The initial tribosystem with a total of ca. 152000 atoms is shown in Fig. 9b. Before performing sliding simulations, the surfaces were annealed according to the procedures adopted from³⁹. Note, that our construction scheme generated initial tribo-surfaces exhibiting a roughness on the granular level (Fig. 9b) covered with a thin layer of sp^2 and sp^1 hybridised atoms (green and cyan spheres in Fig. 9b). The final system size was 7 x 7 x 21 nm³.

Similar to the single asperity collision, the sliding simulation was achieved by freezing the atomic position of a 0.5 nm layer on top and on the bottom of the system. During the whole sliding process the bottom atoms were kept immobile and the top atoms were rigidly shifted with a constant velocity of 30 m/s. While for the single asperity collision the vertical distance between the upper and lower fixed atom region had been kept constant, in the case of the UNCD sliding a barostat with a target normal pressure of 10 GPa was employed by solving a damped Newton's equation of motion for the upper block of rigid atoms with an additional pressurizing force⁴⁰. Two 0.5 nm thick zones in the direct neighborhood of the rigid atom regions were thermalized to room temperature using a Langevin thermostat³⁷. Note, that constant distance and constant pressure simulations only approximate the experimental loading conditions, since in both cases the elastic compliance of the macroscopic tribo bodies were neglected. For large atomistic simulations involving many asperities, the constant pressure simulations more closely approximate the experiments. Therefore, the UNCD simulation was barostated. On the other hand, in the case of single asperity collisions barostating becomes meaningless before the contact between asperities has been established and therefore constant distance simulations were performed.

4.1.3 Setup of shear cell simulations of diamond particles in a-C matrix

Diamond crystallites (without hydrogen termination) were prepared by cutting them to contain only $\{100\}$, $\{110\}$ or $\{111\}$ -surfaces, respectively. Figure 9c displays the three different crystals: a cube with $\{100\}$ surfaces and 1.7 nm edges (1000 atoms), an octahedral-type crystal with $\{110\}$ surfaces and 2.2 nm edges (1377 atoms) and an octahedron with $\{111\}$ surfaces and 2.1 nm edges (1131 atoms). These diamond crystallites were embedded in a matrix of amorphous carbon (of size $3.25 \times 2.5 \times 3.25 \text{ nm}^3$), with a sp^3 -content of approximately 20%. This has been done by superimposing the crystal and a block of a-C from a high temperature quench simulation and removing all a-C atoms that were within a $1.85 \text{ \AA}$ radius sphere around the diamond atoms. We equilibrate these systems at constant volume and a temperature of 300K for 100ps before shearing at a shear rate of 10^{-10} s^{-1} until a shear strain of 500% is reached. The a-C matrix after relaxation had an sp^3 -content of approximately 10%, sp^2 content of 57% and sp^1 content of 33%. Homogeneous shearing was performed using Lees-Edwards boundary conditions⁴¹. In this method the upper and lower periodic images of a constant volume rectangular cell are continuously translated to the right and to the left, respectively. In this way a homogeneous xz strain rate field can be realized.

As a measure for the crystallinity of the diamond particle we use bond angle analysis for all atoms that were part of the original diamond crystal. We classify an atom as crystalline if it has four bonds and all bond angles deviate less than 5° from the expected 109.5° for tetragonal atoms. Note, that this criterion is rather conservative and produced slightly better results compared to other measures of crystallinity such as adaptive common nearest neighbor analysis⁴² or Q-factor analysis^{43,44}.

4.2 Simulation results

4.2.1 Diamond asperity collision

Figure 10 and 11 display snapshots of the diamond asperity collision (colored according to coordination number in Fig. 10 and according to atomic von Mises stress in Fig. 11) starting from the relaxed configuration shown in Fig. 10A. Shortly after formation of the initial contact (Fig. 10B) the contact zone underwent a strong plastic deformation accompanied by

an instantaneous amorphization while the remainder of the asperity atoms exhibit local von Mises strains of up to 15%. During this first stage of the asperity collision atomic von Mises stresses reach peak values of more than 80 GPa (Fig. 11A), around the expected limit from theoretical calculations⁴⁵. This leads to the cleavage of the lower asperity and separation of a diamond nanocrystal: see Fig. 10D for the asperities after the first collision showing an amorphous hydrocarbon layer on the surface and the detached nanocrystal Fig. 10D. Note, that the local stresses are mitigated during the amorphization of the diamond lattice (Fig. 11B).

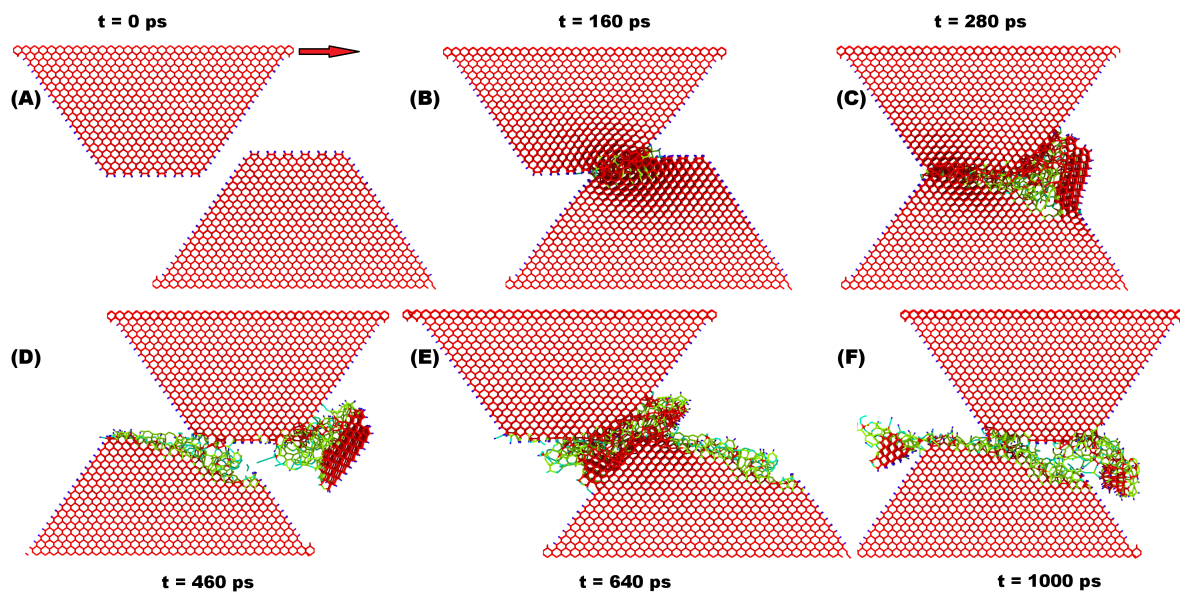


Figure 10:

Snapshots of diamond asperity collision. Colors represent the hybridization of the atoms with red = sp^3 -, green = sp^2 - and cyan = sp^1 -hybridization. The top asperity moves to the right with 14.1 m/s. (A) Initial configuration. (B) First contact is established resulting in zone with plastic deformation and amorphisation. (C) Chipping off of a diamond nanoparticle. (D) After separation of the asperities amorphous material remains on the asperities. (E) The diamond nanoparticle fractures during a second collision. Note, that the upper asperity has left the simulation cell and reappeared from the right due to the applied periodic boundary conditions. (F) Final result with two diamond nanoparticles in contact to an amorphous sp^2 phase (green atoms).

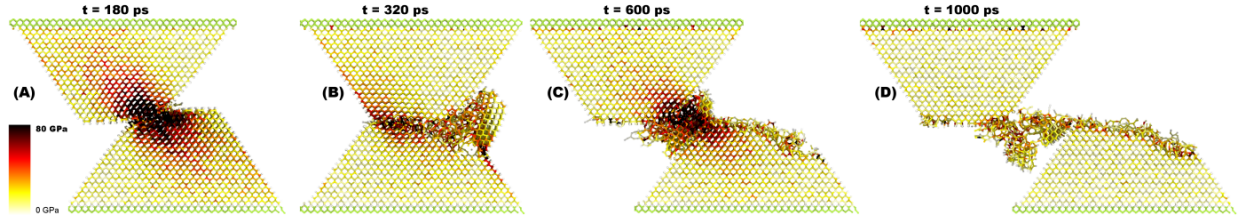


Figure 11:

Atomic von mises stress $\sigma_{v.Mises} = \sqrt{\frac{1}{2}[(\sigma_I - \sigma_{II})^2 + (\sigma_{II} - \sigma_{III})^2 + (\sigma_{III} - \sigma_I)^2]}$, where the σ_I , σ_{II} and σ_{III} denote the principal atomic stresses. A maximum stress of 80 GPa is color coded by black, but single atoms can have slightly higher values. The times in (A) and (C) were selected from the trajectory to represent maxima in the stress evolution.

The amorphous carbon produced by the collision consists of a layer of sp^2 carbon covered with a network of hydrocarbon chains and some long sp^1 carbon chains on the surface. During further sliding the crystalline wear debris can act as an abrasive between the two sliding partners (Fig. 10E) resulting again in an increased atomic stress (Fig. 11C) accompanied by further plastic events during a second asperity collision (increasing the number of sp^2 atoms) and a cleavage of the nanocrystal (see Fig. 10F). The main amorphization happens during the initial collision resulting in the transition of roughly 2000 diamond atoms into the amorphous sp^2 and sp^1 hybridized phase (Fig. 12). This number corresponds to a volume of approximately 10 nm^3 of the original diamond. Repeated collisions show further amorphization during contact of the amorphized surfaces (Fig. 12). Interestingly, the a-C growth behavior in Fig. 12 resembles the amorphization of flat diamond surfaces¹⁵ that show a square root type of growth of the a-C with sliding time. During the following asperity collisions (not shown) the resulting comparably hard nanocrystal slid between the ‘soft’ amorphous carbon surfaces without further reduction in nanocrystal size resulting in the precursor of an $sp^2 + sp^1$ a-C phase with interspersed nanodiamond (Fig. 11D).

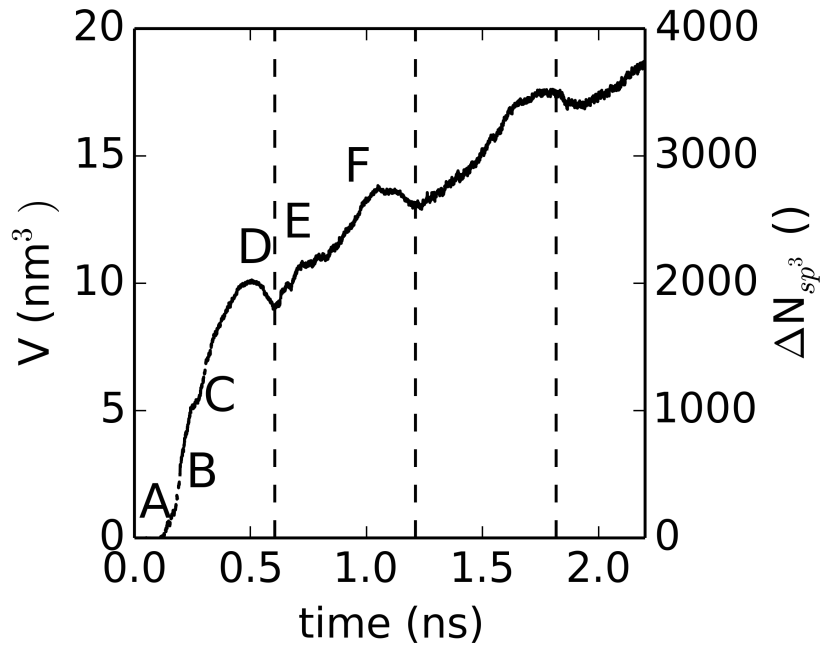


Figure 12:

Evolution of the sp^3 hybridization during the diamond single asperity collision. On the right ordinate the number of atoms that have changed their hybridization from sp^3 to a sp^2 or sp^1 state is shown. On the left ordinate this number has been multiplied by the atomic volume of diamond in order to estimate the diamond volume that has been amorphised during the TPT. The letters indicate the time instants of the snapshots in Fig. 10, apart from A, which was moved to the right to avoid intersection with the ordinate. The dashed vertical lines mark the time of 0.6 ns for one repeat cycle, due to periodic boundary conditions.

4.2.2 UNCD sliding simulation

A further atomistic simulation with two UNCD surfaces in sliding contact was performed in order to investigate the TPT in polycrystalline diamond coatings. Figure 13 displays the evolution of the atomic structure in a cross section of the UNCD tribosystem within the first 14 ns of sliding. Initially, roughness on both surfaces prevents the system from cold welding (Fig. 13, $t=0$ ns), but already after one ns of sliding a dominant asperity has been significantly worn down. This smoothing in combination with the formation of a soft a-C phase (with sp^2 and sp^1 atoms) that fills the tribo gap leads to the establishment of complete contact between both UNCD films after 1 ns (Fig. 13). The a-C phase grows steadily during further shearing of the sample (see times >1 ns in Fig. 13). After 14 ns, a roughly 4.5 nm thick amorphous layer has been formed with 8% sp^3 , 76% sp^2 and 16% sp^1 atoms. The formation of this zone comes along with an increase of the system height (see Fig. 13 in the period of time from 2 ns to 14 ns), since the tribo-induced crystalline-amorphous transition is accompanied by a noticeable expansion of the amorphous phase due to an increase in atomic volume. Similar

amorphization has also been observed for flat single crystalline diamond sliding¹⁵. For comparison, the atomistic structures of diamond (110) surfaces during sliding are also shown in Fig. 13. The comparison with our UNCD results suggests an amorphization rate that is comparable to the rate on the softest diamond single crystal facet.

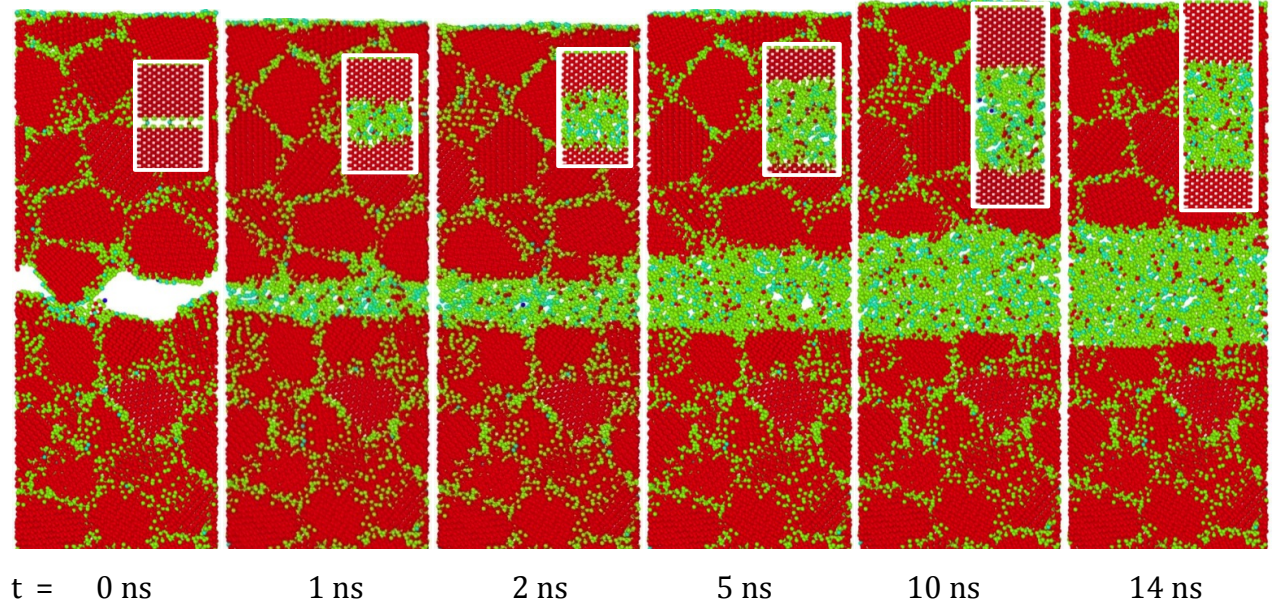


Figure 13:

Evolution of atomistic structure of UNCD in a 1nm-thick slice. Topography smoothing, amorphization and sp^3 -to- (sp^2/sp^1) rehybridization are observed at the sliding interface. Colors represent the hybridization of the atoms with red = sp^3 -, green = sp^2 - and cyan = sp^1 -hybridization. Atomistic structures of single crystalline diamond (110) during sliding at the same length scale and at the same times as in UNCD are also shown in the insets for comparison. In both cases the upper tribo partner slides to the right with 30 m/s. During the 14 ns that are displayed in the UNCD snapshots the upper tribo partner passed 60 times the periodic length of the cell.

4.2.3 Shear cell simulations of diamond particles in a-C matrix

Since experiments and simulations show the creation of diamond nanocrystals embedded in an amorphous matrix we carried out an additional atomistic simulation intended to reveal the stability of the resulting composite. Figure 14a displays the initial configuration and final configuration after an applied shear strain of 500%. These simulations show that for $\{110\}$ and $\{111\}$ surface orientations the diamond crystal degrades only marginally, affecting only the most outmost layers of atoms. The crystal with $\{100\}$ surface orientation deforms significantly exhibiting a significant size reduction, while distributing the originally diamond atoms all through the amorphous matrix.

Fig. 14b shows the evolution of the amount of crystalline atoms during the shear of the whole cell. The drop in crystallinity seems to follow a roughly linear decay. The $\{110\}$ and $\{111\}$ surfaces transform about 5% of atoms. The crystallite with $\{100\}$ surface orientation degrades significantly faster, transforming to around 70% of the original size in a severely deformed environment after 500% strain.

Since the yield stress of diamond exceeds the yield stress of the amorphous sp^2 phase by almost one order of magnitude, plastic flow is restricted to the matrix, while the diamond particles are only affected by the sliding of the matrix atoms on the diamond facets. This causes a mechano-chemical amorphisation as shown by some of us previously¹⁵ for diamond single crystal surfaces.

Therefore, the extremely small amorphisation rate of a polished single crystal diamond $\{111\}$ surfaces and the much faster amorphisation on the single crystal $\{100\}$ surface¹⁵ can explain the observed stability ordering of the $\{111\}$ and $\{100\}$ terminated particles. On the other hand, the high stability of the $\{110\}$ octahedron is at a first sight puzzling since the $\{110\}$ surface shows the highest wear rate during single crystal diamond polishing¹⁵. A glance on Fig. 9c resolves this riddle. By removing a view small $\{111\}$ terraces the $\{110\}$ terminated particle comes very close to a $\{111\}$ terminated octahedron. Actually, exactly this happens during shearing in the amorphous matrix and consequently the amorphisation rate of the initially $\{110\}$ terminated nanodiamond approaches the rate of the $\{111\}$ octahedron (Fig. 14b).

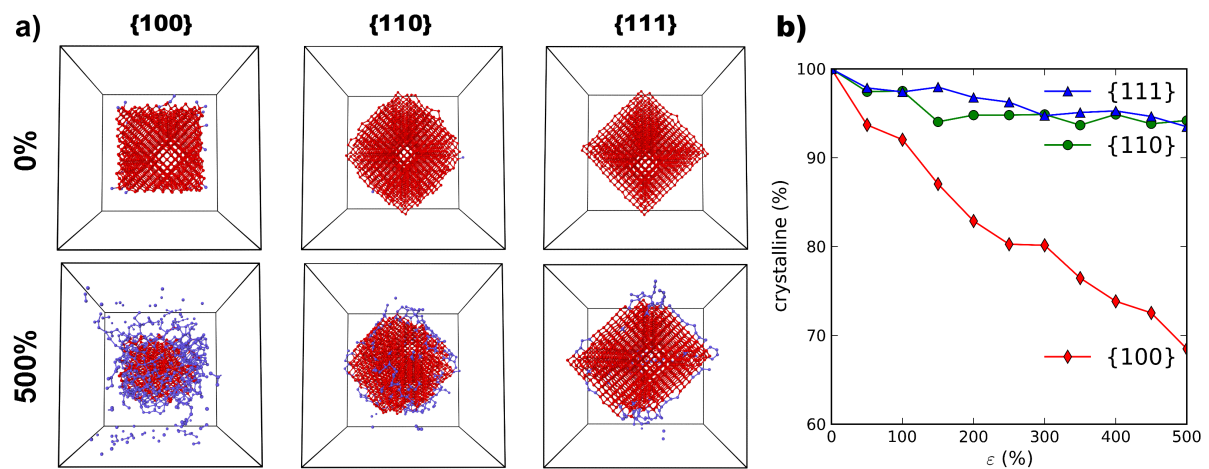


Figure 14: Evolution of a diamond crystal in a homogeneously sheared amorphous carbon matrix. Panel (a) displays the particles from Fig. 9c after embedding into the a-C (atoms within the amorphous matrix are not

shown) and relaxation (top) and after shear with 500% strain (bottom). Red colored spheres represent atoms in a crystalline and blue colored spheres in an amorphous environment. Panel (b) shows the imposed shear strain versus the amount of crystalline atoms in percent of the starting value for three different surface orientations.

5. Discussion and conclusions

A comparison between our experiments and atomistic simulations provides valuable insights into the mechanisms underlying the tribofilm formation between two lubricated NCD coatings. According to our EFTEM analysis that followed the ultralow friction experiments, the tribofilm on NCD consists of an a-C layer containing embedded diamonds nanograins with less than 5 nm in diameter. This agrees well with our single asperity simulations that showed a noticeable amorphization and sp^2+sp^1 increase after only one collision. In addition, a crystalline wear particle was generated during a cleavage process occurring in the final stage of the first collision. Our simulations suggest that these diamond wear particles show a size reduction that depends on the shape of the crystallite and the resulting surface orientations. At least crystals with $\{111\}$ termination are likely to survive extremely high shear strains. It might even happen that non- $\{111\}$ terminated nanodiamonds transform to $\{111\}$ -terminated octahedra during amorphisation – as observed for our simulation of a $\{110\}$ terminated crystal.

The fact that the diamond particle was attached to the a-C and that it was reinserted into the tribological contact in the next collisions lends strong support to a scenario (for both lubricated and dry contacts) where initially two rough diamond surfaces are forced into relative motion leading to severe asperity collisions that flatten the roughness peaks to terraces via a combination of amorphization and fracture processes (see Fig. 15a for an artistic vision of this scenario).

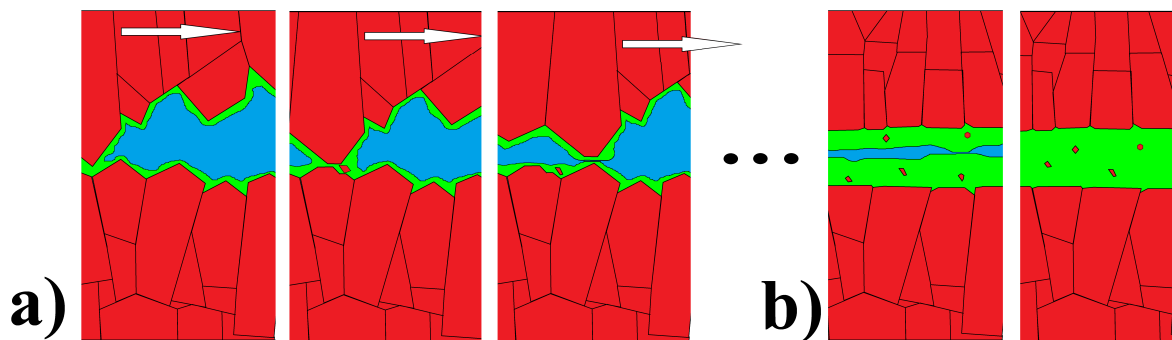


Figure 15:

Artists view of the tribo-induced phase transition and formation of the tribofilm in a lubricated NCD/NCD tribo-system. Red areas represent the sp^3 diamond crystals, black lines are the grain boundaries, green layers are the sp^2 amorphous material. The lubricant is shown as light blue zones in the tribo gap. Panel a) shows an asperity collision that results in the formation of an diamond nano crystal and additional amorphous material. This process is accompanied by reduction of roughness due to the removal of crystal corners of NCD surface grains. In panel b) the resulting structures after many such asperity collisions is depicted. Two situations are highlighted: lubricant can remain between the two amorphous layers leading to low friction (left structure in panel b) or the two layers cold weld resulting in high friction (right structure in panel b).

Our simulations suggest that fracture happens in the early stage of sliding mainly at terrace edges and in the later stage in crystalline debris that are trapped in the a-C between asperities. The resulting initial tribofilm is softer and can be squeezed into the roughness valleys between asperities as has been demonstrated by our UNCD simulations. During further sliding the a-C layer grows further, but now the scenario differs between lubricated and dry conditions (see Fig. 15b). Under dry conditions, both tribopairs cold-weld all the time and a rapid growth of the a-C is expected (see right sketch Fig. 15b) as suggested by the UNCD calculations. In the case of a contact that is lubricated by OH-containing molecules (such as water or glycerol) rapid saturation of dangling surface bonds will prevent further cold welding. Therefore for R-OH lubrication, diamond terraces covered with a passivated sub- μm a-C layer (embedded with nanodiamond and terminated by H and OH groups) easily slide on top of each other resulting in ultralow friction (see left sketch Fig. 15b). However, it is also likely that from time to time the passivation on top of the a-C layers fails leading to the revival of cold welding in localized contact areas. In this case, our UNCD simulation predicts further growth of the a-C layer.

Recently, Zhang and coworkers¹⁶ have reported the formation of an amorphous sp^2 phase (of the order of 100 nm thickness) with interspersed nanodiamonds on coarse-grained diamond layers that were subject to a harsh tribological treatment (with wear rates of 0.6 $\mu\text{m}/\text{h}$) reminiscent of diamond polishing conditions⁴⁶. Strikingly, a similar somewhat thinner a-C layer (with 40 nm thickness) was found on our tribologically loaded NCD coatings although much milder (ultralow friction) conditions were applied. This finding supports our scenario that the a-C forms in dry and lubricated diamond contacts already during topographical

running-in and that the growth rate after running-in is reduced in the ultralow friction regime, since cold welding is efficiently suppressed resulting in a smaller steady state film thickness.

Acknowledgements

MM and JvL are grateful for financial support by the industrial board of the μ TC. LP acknowledges funding by the European Commission (Marie-Curie IOF-272619). TM is grateful for financial support by China Scholarship Council. Calculations were carried out at the Jülich Supercomputing Center (grant hfr09). Visualization was partially carried out with Ovito ⁴⁷.

LTDS-ECL is grateful for the financial support of the French Research National Agency (ANR) for development of diamond coatings. The EFTEM studies were carried out in the Electron Microscopy Lyonnais Consortium (CLYM) <http://www.clym.fr/>.

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