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Evidence of graphitization of diamond-like carbon films during sliding wear

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Diamond-like carbon (DLC) exhibits excellent wear and friction characteristics. Transmission electron microscopy (TEM) has been used to investigate the substructures of as-deposited DLC and DLC debris after wear testing. The as-deposited DLC was found to consist of a dense, three-dimensional network structure with a medium range order (< 3 nm) present. Diffraction pattern analysis showed that DLC was mainly amorphous. Two diffuse diffraction rings with $d_{111} = 0.21$ nm and $d_{220} = 0.12$ nm were observed, suggesting the presence of a short-range cubic diamond structure (sp^3). Morphologically, the wear debris was found to be a discontinuous segregation of carbon particles ranging from nano- to micro-size. Diffraction pattern analysis showed that the debris consisted of graphite (sp^2) and distorted DLC (sp^3). A wear mechanism has been proposed based on the transformation of DLC to graphite. The transformation is related to the frictional energy and includes two stages: hydrogen release from the structure causing lattice relaxation and shear deformation of the DLC structure producing graphite.

1. Introduction

Amorphous hydrogenated carbon, a-C:H, films are very desirable for protective coatings due to their extremely high hardness (2000–9000 kg mm^{-2}), low friction coefficient (0.005–0.1) and superior chemical inertness [1, 2]. Recently, tribological investigations have been performed on diamond-like carbon (DLC) films deposited on various substrates [3–5] and different mechanisms have been proposed to describe the tribological behaviour of DLC films. In several of these studies, the observed low friction coefficient of DLC films has been associated with the formation of a carbon-rich transfer layer on the counterface surface [5–9]. In an alternative mechanism, the low friction coefficients were attributed to the pyrolysis of organic material into graphite [9]. In addition, chemisorption of hydrogen and/or other chemically active species and the formation of a double layer structure and/or micrographitization on sliding interfaces have also been thought to contribute to the low friction of DLC [10–12].

In the present work, transmission electron microscopy (TEM) together with electron diffraction was used to characterize the microstructure of DLC films prior to and after wear testing. The objective was to obtain an insight of possible microstructural changes occurring during the wear process. For the first time, we provide direct evidence of graphitization of DLC occurring during sliding wear. Based on the present experimental evidence, a wear mechanism is proposed to describe the low friction of DLC films.

2. Experimental procedure

Thin DLC films (0.4 μm thick) were deposited on Ti–6Al–4V substrates at room temperature by methane ion-beam deposition (IBD) using a Kaufmann-type ion source. The deposition was conducted at an accelerating voltage of 750 eV and a current density of approximately 2.5 mA cm^{-2}. These experimental conditions have been found to produce high-quality, dense DLC films. Experimental details are given elsewhere [5].

Pin-on-disc wear experiments were conducted on DLC coated discs (50 mm diameter and 5 mm thick) using Ti–6Al–4V alloy as the pin material (9.5 mm diameter, 127 mm tip radius and 20 mm length) under an applied load of 10 N and at a sliding speed of 0.05 m s^{-1}. This loading level produced an initial Hertzian stress of about 70 MPa. All tests were conducted for a total sliding distance of 1000 m and the coefficient of friction was recorded continuously. The tests were carried out in laboratory air (about 30% relative humidity) and at room temperature. Analytical TEM was carried out at 100 keV to characterize the substructure of DLC films prior to and after wear testing. Fine particles of as-deposited DLC film were scratched from the discs using a sharp blade and transferred on to copper grids (400 mesh). Similarly, debris from the wear track region and from the transfer film present on the pin counter surfaces were transferred on to copper grids for TEM examination.

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3. Experimental observations

The as-deposited DLC films were found to be smooth, uniform and free of any visible bulk volume defects. Figs 1a and b present high-magnification bright-field transmission electron micrographs from representative thin sections extracted from as-deposited DLC specimens. It is evident that the film has a mainly featureless microstructure. Detailed analysis showed that the films were composed of a continuous matrix with ultra-fine size features less than 3 nm diameter (these features are discernible in Fig. 1), suggesting a medium-range order. This subject has been reviewed by Robertson [13] and medium-range ordering (in the 1 nm scale) is expected in these type of films.

The corresponding diffraction pattern of as-deposited DLC, Fig. 1c, revealed two diffuse rings, indicative of an amorphous structure. The *d*-spacing of the rings was indexed to be approximately 0.21 and 0.12 nm, corresponding to $(1\,1\,1)_{\mathrm{DLC}}$ and $(2\,2\,0)_{\mathrm{DLC}}$, respectively, indicating a short-ranged diamond-like structure. In crystal diamond, the (1 1 1) and (2 2 0) are the strongest diffractions and correspond to $d = 0.206$ and 0.126 nm, respectively. These results are in agreement with those reported previously on amorphous DLC deposited by r.f. glow discharge [14, 15]. Another interesting feature in the diffraction patterns was that the central spot was larger than usual and it is possible that the strongest (0 0 2) sp^2-graphite reflection was present as a diffuse halo (*d*-0.34 nm) encircling the central spot.

In our previous study [16], Auger, Fourier transform–infrared (FT–IR) and laser Raman spectroscopy were utilized to characterize the present DLC films. It was found that as-deposited DLC is amorphous and composed of a mixture of sp^3/sp^2 carbon–hydrogen bonds. Also, the high hardness measured for as-deposited DLC ($\sim 3000\ \mathrm{kg\,mm^{-2}}$) was attributed mainly to the presence of the sp^3 bonding. The results of that study and the present TEM findings are consistent with previous proposals suggesting that sp^2 and sp^3 sites in the DLC structure tend to segregate into sp^2-bonded small graphite-like clusters (involving fused six-fold rings) that are embedded in a sp^3-bonded matrix [9]. Spectroscopic ellipsometry studies for the present DLC films showed an optical gap $E = 1.6$ eV suggesting about 14 aromatic rings per cluster [16].

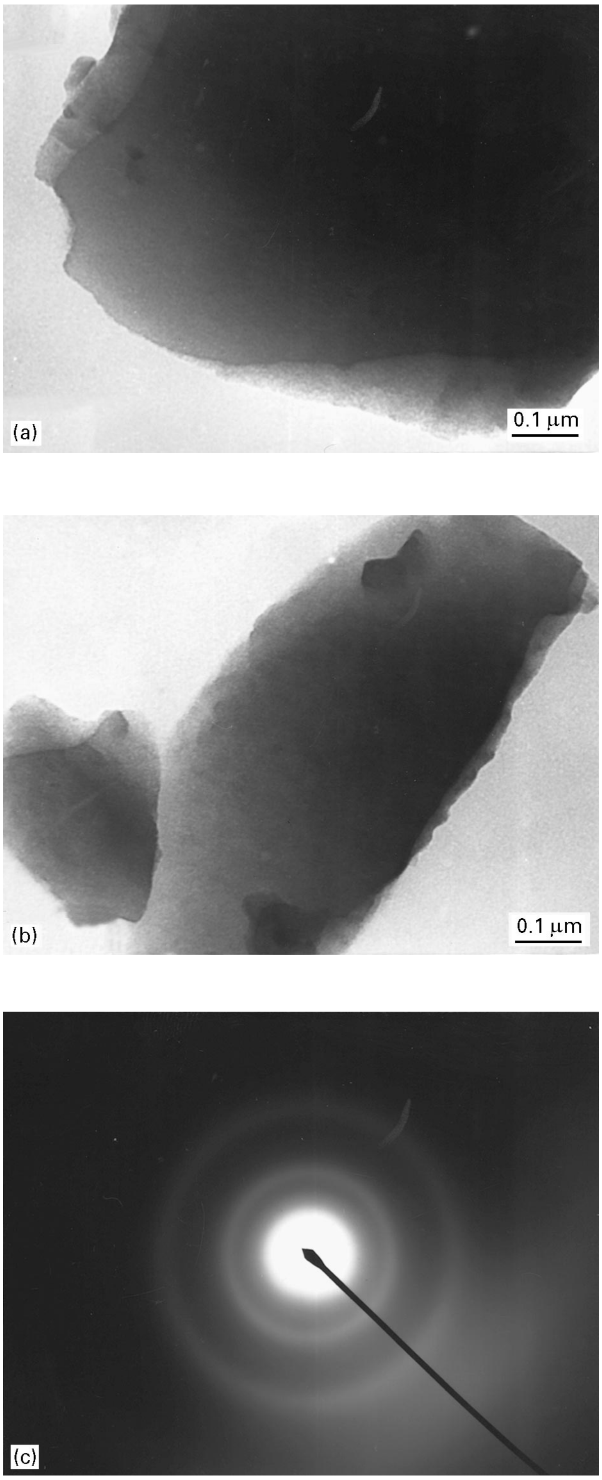

Figure 1 (a, b) High-magnification bright-field transmission electron micrographs of as-deposited DLC film. (c) The corresponding diffraction pattern of as-deposited DLC film.

Typical morphology of debris collected from wear scars and pin surfaces after 1000 m friction testing is shown in Figs 2a and b. The observed debris morphology was distinctly different from that of the as-deposited DLC. The debris was found to be a discontinuous segregation of clusters of various shapes consisting of agglomerated particles ranging from nano- to microsize. The irregular shapes of the clusters were likely the result of friction. A typical diffraction pattern from these clusters is given in Fig. 2c. Mainly the diffraction pattern consists of a strong diffuse ring at approximately 0.33 nm and three faint rings with *d*-spacing approximately 0.21, 0.18 and 0.12 nm, respectively. The values of 0.33 and 0.18 nm are consistent with the (0 0 2) and (0 1 2) diffractions of graphite. The *d*-spacing of 0.21 and 0.12 nm is respectively near the *d*-spacing of $(1\,1\,1)_{\mathrm{DLC}}$ and $(2\,2\,0)_{\mathrm{DLC}}$ and due to their faint and scattered appearance, are considered to evolve from a distorted DLC film structure. The observed characteristics of the diffraction pattern from debris suggested that during sliding, as-deposited DLC film was significantly distorted and most of the DLC has transformed into graphite. The resulting debris is the mixture of distorted DLC and graphite. This aspect was further evidenced by dark-field analysis. Figs 3a and 3b show, respectively, bright- and dark-field images of a section of a transfer layer. The

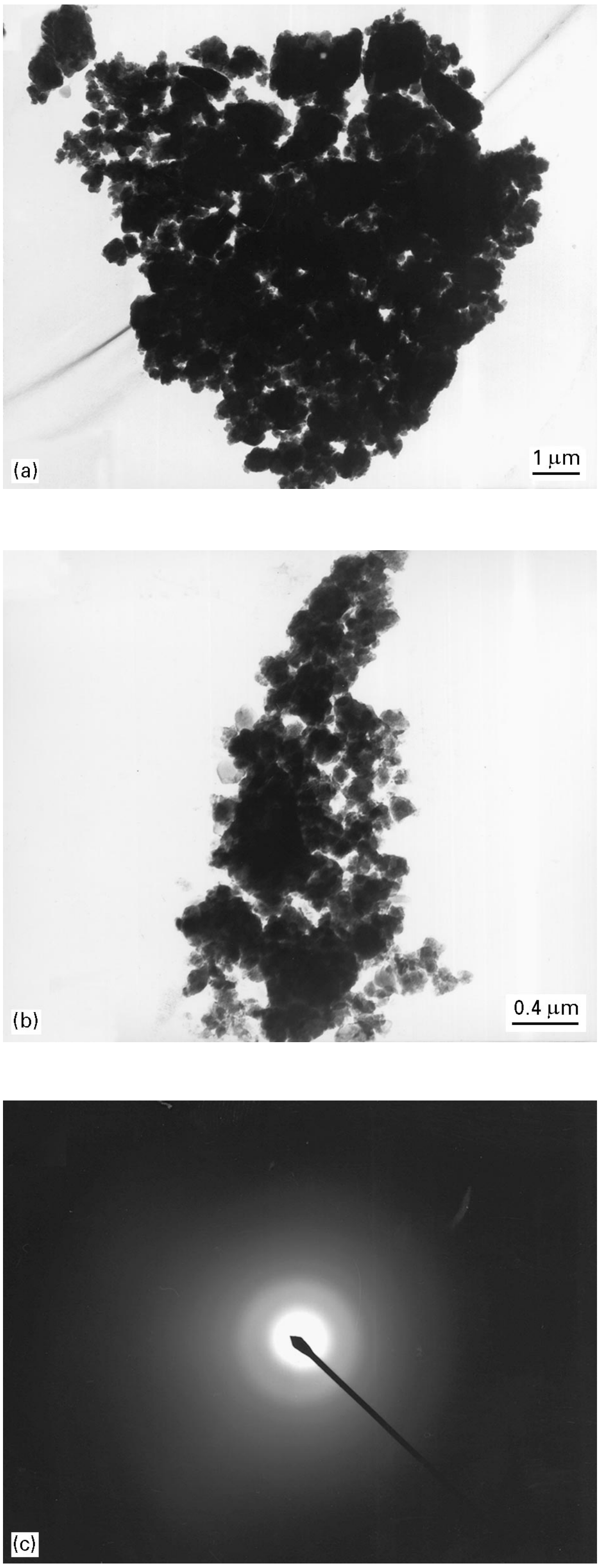

Figure 2 (a, b) High-magnification bright-field transmission electron micrographs of wear debris after 1000 m friction test (10 N, 0.05 m s^{-1} sliding speed). (c) The corresponding diffraction pattern of wear debris.

dark field was obtained by utilizing part of the (0 0 2) diffraction ring. It is evident that small graphite particles (about 5–1.0 nm diameter) are present, Fig. 3b. It is characteristic to note that the graphite particles form in streak-like clusters along the sliding direction. This particular cluster formation suggests that friction-related effects (heat and strain) contribute to the transformation of DLC into graphite. This orientation arrangement of nucleated graphite particles was evident at high magnification observations, Fig. 3c.

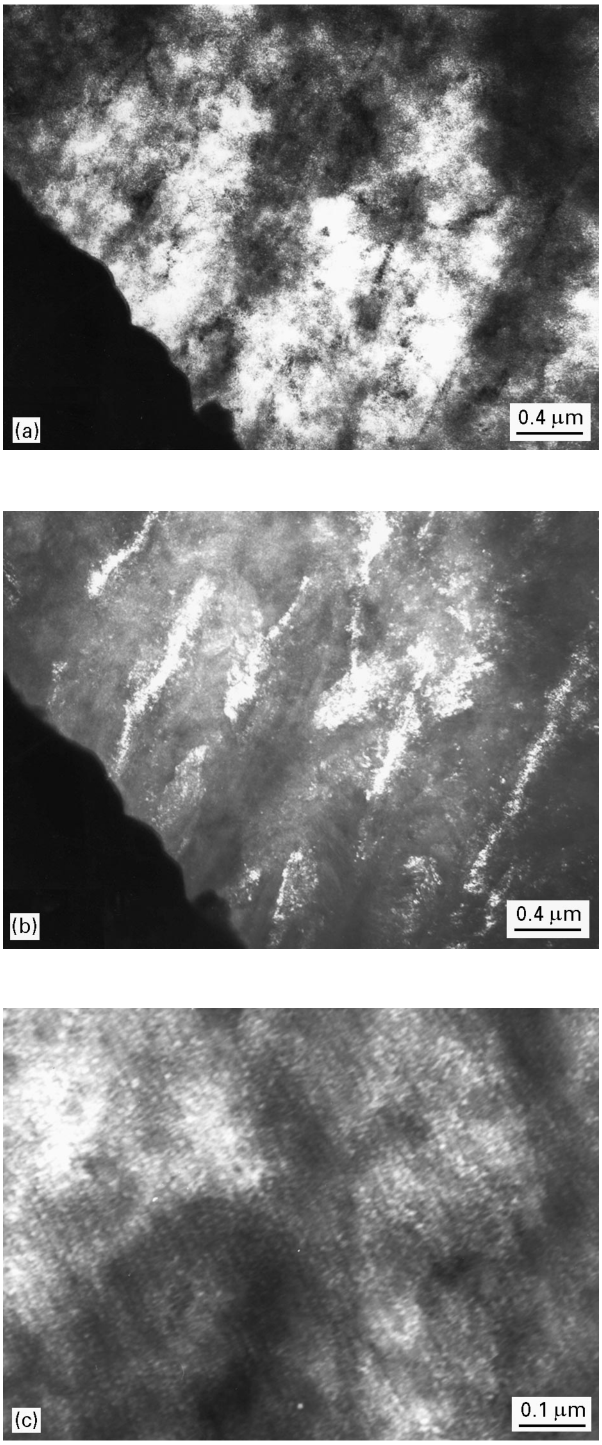

Figure 3 (a) Bright-field image of a portion of the transfer layer. (b) Dark-field image of the same area using part of the (0 0 2) diffraction ring. (c) High magnification of an area in (a) showing orientation arrangement of nucleated graphite particles along the sliding direction.

4. Graphitization of DLC and friction mechanism

As-deposited DLC is thought to be a metastable structure and it tends to transform into stable graphite after an energy barrier is overcome. The present observations show that the process of sliding friction provides the energy required for the transformation of DLC (diamond cubic) to graphite (hexagonal). Previous research showed that the sp^3 carbon structure can be converted to pure sp^2 structure by heating at about 500–600 °C [17]. The internal energy change per unit volume accompanying this process is

$$Q = C_{\mathrm{DLC}}\,\rho\,\Delta T \tag{1}$$

where C_{DLC} is the specific heat of DLC (about 600 $\mathrm{J\,kg^{-1}\,K^{-1}}$), ρ is its density (2.6 $\mathrm{g\,cm^{-3}}$) and ΔT is the temperature raise at which the sp^3 structure is converted into sp^2 structure. From the above data, Q is calculated to be from 741–897 $\mathrm{J\,cm^{-3}}$. The calculated energy range can be considered as an upper limit for the activation energy of the transformation.

The real contact area during friction is determined by the microtopography of the surfaces. According to Hertzian contact theory, the radius, a, of the equivalent circular contact area is given by

$$a = 0.0182\,(P\,D\,C_{\mathrm{E}})^{1/3} \tag{2a}$$

where

$$C_{\mathrm{E}} = (1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2 \tag{2b}$$

P is the nominal external load applied perpendicular to the surface (10 N in the present work), D is the diameter of the pin (254 mm), E_1 and E_2 are the elastic modulii of Ti–6Al–4V and DLC (114 and 350 GPa, respectively), ν_1 and ν_2 are the Possion's ratios of Ti–6Al–4V alloy and DLC (0.321 and 0.3, respectively). Thus, a is calculated to be about 5.35×10^{-6} m. The work due to friction at the contact area per rotating cycle can be estimated by

$$W = Pf\,(2a) \tag{3}$$

where f is the friction coefficient (0.18 in the present case). From Equation 3, W is calculated to be about 1.93×10^{-5} J. Assuming a perpendicular cylinder beneath the contact asperity going through the thickness of the DLC film, the required energy for graphitization, E, of a depth, d, of this cylindrical volume can be given by

$$E = \pi a^2\,d\,Q \tag{4}$$

For the present case, Equations 3 and 4 show that, in principle, the energy produced by friction may be sufficient to transform the entire DLC thickness under the contact area. However, the amount of the transformed material will depend on the kinetics of the transformation.

The particular pattern exhibited by the graphite particles formed during wear, indicates that nucleation occurred locally at asperity contacts where high flash temperatures may have developed. Fig. 3 shows that the graphite streaks extend about 0.2–1 μm in length and the individual graphite nuclei are a few nanometres in size. The small graphite particle (nucleus) size suggests that temperatures higher than the transformation temperature lasted for a short period of time and their occurrence can be attributed to flash temperature at asperity contacts. If the observed length of the graphite streaks is taken as a rough measure of the contact area at individual asperities, then the flash temperature is estimated to be much higher than 600 °C [18] and is consistent with the previous suggestion.

Experimental observations [19] show that during friction, a carbon-rich transfer layer forms on the pin surface. Because the transfer layer is mainly composed of DLC [19], the tribological contact is modified from that of Ti–6Al–4V/DLC to that of DLC/DLC and significant temperature rise may result at the contact due to the low thermal conductivity of DLC. Differential scanning calorimetry experiments have showed that at about 450 °C, release of hydrogen atoms from DLC lattice occurs [20]. Also, thermal annealing experiments by Dischler [21] on IBD DLC films showed that hydrogen begins to evolve at 300 °C while the sp^2 fraction increases at 400 °C. It is believed that hydrogen atoms, introduced by the deposition process, play a critical role in promoting and stabilizing sp^3 tetrahedral bonds in the DLC structure [22]. It is also suggested that several hydrogen atoms are compressed into one vacancy of aromatic domain in the DLC lattice [23], distorting the diamond cubic lattice. In the present work, the lattice parameter of DLC was found to be 0.364 nm, which is larger than that of real diamond (0.357 nm). During wear testing, a friction-induced annealing process is expected probably to be able to result in gradual hydrogen liberation from the DLC lattice and reduction of the DLC lattice distortion in aromatic domains. The $(1\,1\,1)_{\mathrm{DLC}}$ plane of diamond cubic structure and the $(0\,0\,2)_{\mathrm{GR}}$ graphite (hexagonal) plane have identical atomic arrangements and a small difference in the atomic spacing, 0.257 nm for $(1\,1\,1)_{\mathrm{DLC}}$ and 0.246 nm for graphite. After hydrogen is released from DLC, the extent of the sp^3 C–H bonding is reduced, resulting in sp^2 covalent bonding causing a decrease in the $(1\,1\,1)_{\mathrm{DLC}}$ interplanar distance and the atomic spacing on $(1\,1\,1)_{\mathrm{DLC}}$, that becomes more coherent to $(0\,0\,2)_{\mathrm{GR}}$. Thus, the coherency between these two planes with identical atomic arrangement after hydrogen release, more than likely provides the prerequisite for the transformation of DLC lattice to graphite lattice. This seems to be supported by the electron diffraction patterns, indicating that the formed graphite has strong (0 0 2) nucleation preference and the particular orientation arrangement of the graphite particles, Fig. 3c.

The transformation of DLC to graphite may also be facilitated by the shear stresses existing in the surface layer. The friction-induced shear forces cause strain parallel to the contacting surfaces. This strain energy produced by friction can be used to accomplish the necessary deformation for the transformation of DLC to graphite after the release of hydrogen atoms. The stacking of $(1\,1\,1)_{\mathrm{DLC}}$ and $(0\,0\,2)_{\mathrm{GR}}$ planes are in an ABCABC… and ABAB… sequence, respectively. If layer C slides across layer B, the layer C tends to coincide with layer A and the stacking sequence becomes ABAB…. As discussed above, after the release of hydrogen atoms from the DLC lattice, the $(1\,1\,1)_{\mathrm{DLC}}$ and $(0\,0\,2)_{\mathrm{GR}}$ become coherent and the shearing on the $(1\,1\,1)_{\mathrm{DLC}}$ plane probably produces a hexagonal layer by changing the stacking sequence of atoms on the layer. Thus, wear-induced graphitization is expected to result in microcrystalline graphite with graphite layers stacked in an arbitrary sequence and orientation.

In our previous study [19], pin-on-disc experiments conducted on DLC films produced by methane IBD showed three distinct friction regimes. Initially, a break-in period with continuous decreasing friction coefficient appears, followed by an intermediate constant friction plateau of a relatively short duration, that precedes a low friction coefficient ($f < 0.05$) steady state stage. Considering the graphitization process discussed above, the initial reduction in the friction coefficient during the break-in stage can be attributed to the gradual release of hydrogen atoms from the sp^3 lattice producing an easily sheared structure. The intermediate constant friction plateau can be related to the formation of the transfer layer with some small-scale graphitization at "hot spots". The low friction steady state stage can be related to the extensive graphitization of the transfer layer. The low shear strength between hexagonal planes in graphite (due to weak Van der Waals forces) can account for the low friction coefficient and ultra-low wear rate (less than $1.6 \times 10^{-9}\ \mathrm{mm^3\,mN^{-1}}$) observed in this stage [19].

5. Conclusion

The structure of as-deposited DLC and debris produced during friction have been investigated using transmission electron microscopy. As-deposited DLC exhibited a dense and featureless microstructure. Electron diffraction pattern analysis revealed a mainly amorphous structure with evidence of short-range sp^3 diamond cubic domains. Wear debris was found to consist of a segregation of discontinuous particle clusters. Diffraction analysis showed that the debris composed of graphite and distorted DLC. The analysis, along with the morphology of the formed graphite, indicate the graphitization of DLC occurred at "hot spots" during asperity contact. The transformation is suggested to proceed with a precursor hydrogen atom release stage and shear deformation that converts the $(1\,1\,1)_{\mathrm{DLC}}$ into $(0\,0\,2)_{\mathrm{GR}}$ planes facilitating the nucleation of graphite. The low friction observed experimentally during wear of DLC is attributed to low shear strength of the hexagonal graphite planes.

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