Tribological behaviour of different diamond-like carbon materials

E. Liu a,*, B. Blanpain b, X. Shi a, J.P. Celis b, H.S. Tan a, B.K. Tay a, L.K. Cheah a, J.R. Roos b

a School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Nanyang, Singapore 639798
b Department of Metallurgy and Materials Engineering, Catholic University of Leuven, de Croylaan 2, B-3001 Leuven, Belgium

Received 5 January 1998; accepted 30 March 1998

Abstract

This paper comparatively studies the tribological behaviour of different types of diamond-like carbon (DLC) coatings in a reciprocating sliding wear test. The results are interpreted in terms of structure and surface morphological characteristics. At the beginning of each reciprocating sliding wear test, the higher coefficient of friction of the DLC coatings reflects the original surface conditions of contacting counterfaces, whereas the low coefficient of friction achieved under the steady regime is linked to the presence of wear debris and an enlarged real contact area. sp2 carbon bonding has been related to the occurrence of a higher coefficient of friction and surface damage of DLC materials compared to bulk diamond. The a-C coatings and ta-C films have a lower coefficient of friction at the steady regime than the a-C:H coatings, possibly due to a significant amount of hydrogen in the a-C:H coatings. © 1998 Elsevier Science S.A.

Keywords: Diamond-like carbon (DLC); Reciprocating sliding; Tribology

1. Introduction

For single crystal diamonds with a smooth surface, the mechanical and tribological properties vary depending on the crystallographic planes and orientations [1–3]. For polycrystalline diamond coatings, not only the crystal orientation but also the surface morphology, coating thickness, and presence of non-diamond carbon phases may influence the friction and wear behaviour [4–6]. Concerning diamond-like carbon (DLC) materials, some important aspects should be considered. DLC materials are amorphous. The amorphous carbon (a-C) coatings mainly contain a mixture of sp3 and sp2-bonded carbon, the hydrogenated amorphous carbon (a-C:H) coatings also contain a significant amount of hydrogen, whereas the tetrahedral amorphous carbon (ta-C) films mainly contain sp3-bonded carbon atoms (over 80%) [7]. These characteristics may cause the tribological behaviour of DLC materials to be considerably different from that of bulk diamond. DLC may, in theory, have optical, electrical and mechanical properties similar to those of diamond. However, the graphite particles ejected from the arc spot in a cathodic arc process without magnetic filters are deflected, owing to numerous elastic collisions with the internal wall of the plasma and substrate [8]. For the ta-C films deposited in a cathodic vacuum arc process with magnetic filters [9,10], the macroparticles can be effectively filtered. The properties of ta-C films have been correlated with the energy of the incident carbon ions during deposition [7,11–13]. For the a-C:H coatings, the hydrogen content must be a key factor. Zaidi [14] reported that DLC films containing hydrogen have a longer lubricating life with a low coefficient of friction and a low wear rate in an inert environment, whereas films without hydrogen show a low friction coefficient in an air environment. A graphitic transfer layer or a third-body layer formation containing hydrocarbon has been related to a low coefficient of friction.

This paper investigates the tribological behaviour of DLC materials in a reciprocating sliding wear test. The results are interpreted in terms of structure and surface morphological characteristics of the samples.

2. Experimental

Three types of DLC coatings, namely a-C coatings by cathodic vacuum arc ion plating without magnetic
filters, a-C:H coatings by r.f. plasma-enhanced CVD, and ta-C films by a filtered cathodic vacuum arc, were investigated. A combustion flame (CF) diamond coating, a synthetic bulk diamond (1b) with a polished (100) surface, and a highly ordered pyrolytic graphite (HOPG) sample were used as references. The deposition conditions of DLC coatings as well as the CF coatings are summarized in Table 1.

A reciprocating sliding wear test set-up with a linear oscillatory displacement was used to evaluate the tribological behaviour in a localized area. The device consists of an xyz-positioning system. A ball-on-disk geometry was adapted for the simulation of reciprocating sliding wear test. The details of the reciprocating sliding wear test configuration used have been described elsewhere [15]. Using this set-up, the linear contact displacement, normal contact force, and responding friction force were measured as a function of time over the duration of one reciprocating sliding cycle, and the data were recorded on-line.

The sample surface oscillated against a 10-mm-diameter corundum ball in a laboratory atmosphere (20°C, RH 50%) without lubrication under the following testing conditions: a normal load of 2 N, an oscillatory displacement stroke of 100 nm, a vibration frequency of 8 Hz, and a number of reciprocating sliding cycles in the range of 10,000 – 500,000. Under this set of testing conditions, a gross-slip regime was active. The coefficient of friction, taken as being equal to the average friction coefficient, was derived from the integration of the area enclosed in each tangential force-displacement loop divided by twice the displacement stroke and the normal load.

With the reciprocating sliding test, the static friction and dynamic friction can be extracted from each tangential force-displacement loop as shown in Fig. 1. The friction regime can then be determined by the relationship between the static friction and the kinetic friction with respect to sticking time or sample surface speed [16], or by a relative change in the static friction with respect to sticking time [17].

A atomic force microscopy (AFM), operated in a contact mode (NanoScope III, Digital Instruments) or in a tapping mode (Dimension-3000, Digital Instruments), was used to identify the morphological characteristics of the samples both before and after exposure to the reciprocating sliding wear. The sample surface roughness, such as R_a and R_t, was evaluated according to the ISO and DIN standard by surface profilometry (Taylor-Hobson and Tencor P-10). The roughness R_w was also measured in a square area by AFM for comparison. The surface morphological characteristics of the samples are shown in Table 2.

A micro-Raman Spectroscope with a Spectra Physics Ar-ion laser (S-3000, Jobin-Jvon) was used to characterize the coating structure. The laser output power was in the range of 10–20 mW, and the laser wavelength was 514.5 nm. The laser beam was focused on the sample surface using an optical microscope with a magnification of 100 × (laser spot size ~2 nm).

The hardness and Young’s Modulus of DLC films were measured using a nanoindentation technique (Nanoincider I and II, NanoInstruments). With Nanoindentor II, the hardness and E-modulus were determined from the unloading segment on a load-displacement loop. With Nanoindentor I, a continuous stiffness measurement was performed to measure the hardness and E-modulus. A displacement control mode with a

<table>
<thead>
<tr>
<th>Parameter</th>
<th>a-C</th>
<th>a-C:H</th>
<th>ta-C</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar (plasma gas)</td>
<td>10⁻³ – 10⁻² mbar</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CH₄ (reactive gas)</td>
<td>—</td>
<td>1.7 Pa</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O₂ (reactive gas)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5 l min⁻¹</td>
</tr>
<tr>
<td>C₂H₂ (reactive gas)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5 l min⁻¹</td>
</tr>
<tr>
<td>Södfate</td>
<td>M₂ (HSS)</td>
<td>M₂ (HSS)</td>
<td>% water</td>
<td>WC-Co</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>&lt;200°C</td>
<td>&lt;200°C</td>
<td>Room temperature</td>
<td>850 ± 20°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>10⁻¹ – 10⁻² mbar</td>
<td>1.7 Pa</td>
<td>10¹ – 10¹ Torr</td>
<td>760 Torr</td>
</tr>
<tr>
<td>Deposition duration</td>
<td>~2 h</td>
<td>~2 h</td>
<td>~3 min</td>
<td>~1 h</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>—</td>
<td>300 V</td>
<td>80 V</td>
<td>—</td>
</tr>
</tbody>
</table>
and 420 GPa, respectively. 

Y and E-modulus of about 8 GPa and 100 GPa, and the which corresponds to the first surface conditions of the develops to some extent, which indicates that such films ning and the end of each reciprocating sliding wear test weak features, due to a much higher fraction of sp

3 structure and mechanical properties. The ta-C films have carbon contamination [6 ].[19]. The D-peak for the a-C:H is more significant than 12 GPa [20].

The actual ion energy reaching the substrate surface can be calculated by: \( E = e(V_i - V_p) \), where \( e \) is the electron charge, \( V_i \) is the plasma potential, \( V_p \) is the substrate bias voltage, and \( E_b \) is the original ion energy in the plasma. The sp3 fraction may be increased to about 85% at the optimal ion energy, for instance, about 95 eV in this study. Therefore, the high mechanical properties can be achieved. However, a high residual internal stress exists in the ta-C films containing a high fraction of sp3 carbon bonding, for example, up to 12 GPa [20].

The coefficients of friction of DLC coatings and reference samples are shown in Fig. 4. The tangential force-displacement loops corresponding to the begin ning and the end of each reciprocating sliding wear test for the samples used in this study are shown in Fig. 5.

For the bulk diamond and CF diamond coating, the coefficients of friction are highest during the first cycles, which corresponds to the first surface conditions of the counterbodies in the contact [Fig. 4(b)]. Then, the coefficients of friction rapidly decrease to steady state values. Compared to the bulk diamond, the higher coefficient of friction of CF diamond coating at the steady regime is due to the considerable sp3-bonded carbon contamination [6].

For the a-C and a-C:H coatings at the beginning of each reciprocating sliding wear test, the coefficient of friction is also highest due to the same reason as for the diamond materials. Then, the coefficient of friction rapidly decreases to the minimum value of about 0.1 for the a-C:H coating or to a steady-state value for the a-C coating. The minimum value for the a-C:H coating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness, ( R_a ) (nm)</th>
<th>Roughness, ( R_s ) (nm)</th>
<th>Thickness (nm)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C:H</td>
<td>0.037 ± 0.003 (0.007)</td>
<td>1.39 ± 0.37</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>a-C</td>
<td>0.21 ± 0.06 (0.12)</td>
<td>3.51 ± 1.45</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>ta-C</td>
<td>0.023 ± 0.003 (0.008)</td>
<td>0.19 ± 0.09</td>
<td>0.1</td>
<td>—</td>
</tr>
<tr>
<td>CF (100) diamond (45° to polish lines)</td>
<td>0.015 ± 0.004 (0.002)</td>
<td>0.21 ± 0.12</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Conandum ball</td>
<td>0.014 ± 0.003 (0.006)</td>
<td>0.15 ± 0.06</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Ra values in parentheses were obtained from the AFM measurements.

Table 2
Surface morphological characteristics of the samples

74

may be understood as follows. After the maximum frictional resistance at the beginning of reciprocating sliding wear test is overcome, the wear debris and smoothened counterfaces can reduce the friction force. Once the contacting surfaces are smoothened and if no material degradation occurs during the first cycles, the interaction energy at the interface between the counterfaces is expected to be still relatively lower, which can be considered as surface passivation. The interaction of hydrogen with oxygen at the contacting interface is therefore overshadowed. For the following hundreds of cycles, the surface-contacting conditions like temperature and surface-contacting geometry will gradually reach an equilibrium state. At this stage, the passivation surface layer gradually disappears due to the wear induced by the counterbody. The energy at the interface increases, which leads to a stronger interaction between the counterfaces. The interaction between hydrogen and oxygen is also expected to be stronger. The coefficient of friction therefore increases and enters the steady regime. The a-C:H coatings have a coefficient of friction of about 0.14, and a-C coatings have a coefficient of friction of about 0.08. The following gradual increase of coefficient of friction of the a-C:H coatings under the steady regime is possibly due to the coarsening effect in the real contact area or continuous surface depassivation effects. The lubricating effect of wear debris is therefore weakened.

The friction of a-C coatings at the steady regime is lower than the a-C:H coatings because the a-C coatings mainly contain a mixture of sp³ and sp²-bonded carbon, whereas the a-C:H coatings include a large number of hydrogenated sp³ bonds. Some hydrogen can also exist freely in the coatings. Hydrogen in the a-C:H coating may be responsible for its higher friction than that of the a-C coating.

The a-C coatings may behave like polycrystalline diamond materials with considerable sp² contamination such as the combustion flame diamond coatings [Fig. 4(b)]. Under the same wear testing conditions, the
The coefficient of friction of a-C coatings is higher than that of high-purity diamond materials such as polished (100) bulk diamond. If a completely sp\textsuperscript{3}-bonded a-C coating were to be produced, it may be expected that the friction of such a coating would be comparable with that of high-quality bulk diamond materials. However, with metastable deposition conditions, some sp\textsuperscript{2} contamination is almost always involved in DLC coatings even in the diamond coatings.

The friction behaviour of the ta-C films shows some difference from that of the a-C and a-C:H coatings. After the first few cycles, the coefficient of friction increases to the maximum value, then decreases with increasing number of sliding cycles. The first increase of coefficient of friction is due to the composite effects of surface roughness and film structure. As indicated in Table 2, the ta-C films have a smoother surface than the a-C coatings. It is reasonable to expect that the coefficient of friction of ta-C films is lower than that of the a-C coatings at the onset of the tests. Further, a very thin top layer of sp\textsuperscript{2}-bonded carbon is expected [21]. Such an sp\textsuperscript{2} layer can be easily scratched and plays a lubricating role to compensate the effect of surface roughness, which leads to an even lower coefficient of friction at the beginning of the reciprocating sliding wear test. With the removal of the sp\textsuperscript{2} layer, the contribution from the surface roughness becomes significant. Thus, the coefficient of friction increases during the test. According to Hertz's theory [22, 23], the real contact pressure between the two counterfaces in the contact can be beyond the compressive strengths of both materials at some contacting points. The surface damage of both ta-C film and corundum counterbody can be expected. Therefore, the produced wear debris and the increased true area of contact lead to the observed decrease in coefficient of friction with the sliding cycles.

The continuous decrease in coefficient of friction up to the steady state during the following cycles for the ta-C films is a result of the accumulation of wear debris and continuous increase in real contact area between the two counterfaces (Fig. 6(a)).

As reported in Ref. [20], the ta-C films used in this study can contain sp\textsuperscript{3}-bonded carbon atoms up to 85%. The mechanical and tribological properties of ta-C films should, in theory, be closer to those of bulk diamond than the a-C coatings. However, no considerable difference of frictional behaviour between the ta-C films and the a-C coatings under the steady regime of wear tests was observed. It should be noted that the ta-C films used in this study are very thin (up to 100 nm in thickness), as shown in Table 2. As demonstrated in Ref. [20], the measured mechanical properties such as hardness and E-module of the ta-C films may have been underestimated due to the effect of Si substrate on indentation measurement. Hence, the Si substrate may influence the tribological behaviour of ta-C films under the steady regime, which has possibly resulted in a higher measured coefficient of friction.

In order to test the effects of sp\textsuperscript{2}-bonded carbon on the tribological behaviour of DLC coatings, a HOPG graphite sample was used in this tribological investigation. A freshly cleaved atomically flat (0001) surface was used.

The general tendency of frictional behaviour of HOPG is significantly different from that of diamond and diamond-like carbon materials [Fig. 4(b)]. At the beginning of the test, the friction coefficient is lowest. Then, it continuously increases with reciprocating sliding cycles. Under the steady regime, a coefficient of friction of about 0.33 is maintained, which is much higher than that of the diamond and DLC materials.

The lowest coefficient of friction of HOPG at the beginning of wear test is due to the atomically smooth low-index basal plane with a low energy [24, 25]. When a basal plane is damaged, edge sites with high indices can come into contact with the counterbody, which, together with surface roughening, adhesive wear and
Fig. 5. On-line recorded tangential force–displacement loops corresponding to the beginning and end of each reciprocating sliding wear test for the samples used in this study.
abrasive wear, contribute to the increasing coefficient of friction. Both the a-C and a-C:H coatings were damaged during the wear tests as shown in Fig. 6(b, c). The sp²-bonded carbon in both coatings or hydrogen contained in the a-C:H coating may be responsible for such damage. Such behaviour may also be interpreted in terms of the tribological behaviour of both diamond and graphite materials. It was found that CF diamond coatings were scratched during a reciprocating sliding wear test [6], which can be attributed to an imposed shear stress beyond the compressive strength of these materials. The compressive strength of the diamond crystallites in the CF coatings may have been reduced due to a significant number of sp²-bonded carbon atoms trapped in the diamond crystals as identified from the Raman spectroscopic measurements. The tribological behaviour of DLC materials is therefore in between that of diamond and graphite materials, depending on the content of sp²-bonded carbon.

Supposing that a single diamond crystal is in contact with the corundum counterbody during a reciprocating sliding wear test, Hertz’s theory [22,23] can be used to analyse such a contact couple. For the ease of discussion, the diamond crystal is simplified as a smooth semi-sphere with a radius, \( R_1 \), counteracted by a smooth corundum ball with a radius, \( R_2 \). Under the action of a normal force, \( F_N \), a circular area of elastic contact can be formed with a radius, \( a \): \[
a = \left( \frac{3F_N}{4E_1} \right)^{1/3},
\]
and a maximum pressure applied at its centre, \( p_0 \): \[
p_0 = \frac{3F_N}{2\pi a^2},
\]
with \( 1/R_0 = 1/R_1 + 1/R_2 \), \( 1/E_2 = (1−n_2^2)/E_2 + (1−n_1^2)/E_1 \), where \( E_1 \) and \( n_1 \) are the elastic modulus and Poisson ratio of diamond, and \( E_2 \) and \( n_2 \) the elastic modulus and Poisson ratio of corundum, respectively.

For example, for a CF diamond coating with crystallites ranging from 3 to 10 \( \mu m \), \( E_1 = 1141 \) GPa, \( E_2 = 300 \) GPa, \( n_1 = 0.07 \), \( n_2 = 0.24 \), and 62 GPa < \( p_0 \) < 141 GPa at \( F_N = 2 \) N. The compressive strength is 2.5 GPa for the corundum [26] and 10 GPa for the bulk diamond [27]. It follows that elastoplastic deformation on the contacting counterfaces or brittle fracture of diamond crystallites may occur for the single asperity contact model under the present wear test conditions.

The other limiting situation is that the diamond sample surface is extremely flat, so a smooth ball on a rigid smooth plate model can be introduced as: \( R_0 = R_2 \). Therefore, \( p_0 < 1 \) GPa, which is certainly lower than the compressive strengths of both corundum and diamond materials. It means that the pure elastic contact holds valid only in the case of the nearly ideal flat diamond surface and a smooth corundum counterbody surface. In fact, the surface conditions of the samples...
used in this study are in between a smooth surface and a single asperity, and even the corundum counterbody surface has a roughness (Table 2). The realistic maximum pressure should therefore be considerably higher than that derived from the smooth plate against a smooth ball model. The elastic moduli of DLC materials are much lower than that of pure bulk diamond. Thus, the compressive strengths of DLC materials are expected to be also much lower than that of pure bulk diamond. However, once the surfaces in the contact start the plastic deformation or are scratched, the high contact pressure can be reduced immediately.

It should be noted that materials with a lower elastic modulus have, in general, a lower elastic limit strength, as in the case of a-C, a-C:H, and HOPG samples. At the initial stage of the wear test, the contact asperities on the surface of these materials can be first plastically deformed, and then wear can take place. From Eq. (2), it seems that \( p_f \) is low when the elastic modulus of DLC materials is low under the assumption that all other contact conditions are kept the same. However, \( p_f \) can be greater than the elastic limit strength of these materials. Therefore, more wear debris is expected, and, in fact, considerable wear on these materials has indeed been observed. However, the mechanisms of production of wear debris seem to be different. For the a-C coating, blackish wear debris has been observed, which can be attributed to graphitic particles trapped in the coating during deposition. For the a-C:H coatings, no clear evidence of debris has been found, but a deep wear scar was noticed. The oxidation of carbon and hydrogen could be the reason for less wear debris being produced on the a-C:H coating, whereas for the HOPG, a significant amount of material removal from the HOPG and materials transfer from HOPG to corundum counterbody are due to abrasive and adhesive wear mechanisms. Since the ta-C films are quite thin, little wear debris from the ta-C materials has been resolved. Its wear mechanism could be in between that of diamond and a-C coatings.

Fig. 5 summarizes the tangential force change from cycle 2 to the end of each test on the samples tested. The higher tangential forces at cycle 2 for samples such as the CF diamond coating and a-C coating, are due to a rougher original surface (Table 2). The polished (100) diamond, ta-C film, HOPG and even a-C:H coating show a relatively low friction at the beginning, which is attributed to their smooth surfaces. Different wear test cycles were used to test different samples due to the film thickness consideration.

It can be clearly seen that the friction forces of CF and a-C coatings significantly decrease, the change of friction force of (100) diamond, ta-C film, and even a-C:H coating is not considerable, whereas the friction force abruptly increases to a very high value for the HOPG sample.

4. Conclusions

The tribological behaviour of diamond-like carbon materials has been investigated in terms of structure and surface morphological characteristics of materials in ambient air.

At the beginning of each reciprocating sliding wear test, a high coefficient of friction of the DLC coatings reflects the original surface conditions of contacting counterfaces, whereas the low coefficient of friction achieved under the steady regime is linked to the coating structure, the presence of wear debris, and an enlarged real contact area.

The surface damage on the DLC-coated samples, caused by the corundum counterbody in the wear tests, can be attributed to the sp2 contamination in these coatings.

Under the same testing conditions, the a-C:H coatings show a higher coefficient of friction than the a-C and ta-C materials due to a significant amount of hydrogen.
in the a-C:H coatings. The differentiation of sp bond structures between the a-C and the a-C:H coatings is also responsible for the different tribological behaviour of these two materials.

The differences between the mechanical properties and tribological behaviour of a-C and those of the ta-C are mainly caused by different amounts of sp3-bonded carbon atoms in these two materials.

Acknowledgement

The authors would like to thank Dr E. Dekempeneer (VITO, Belgium), Dr F. Lo¨zer (RWTH, Germany), Dr A. Alahelisten (Upssala University, Sweden), and Ir. L. Vermeyen (WTOCD, Belgium) for providing DLC or diamond samples. B. Blanpain is a postdoctoral fellow with the Fund for Scientific Research—Flanders.

References

