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Toward Low Friction in High Vacuum for Hydrogenated Diamondlike Carbon by Tailoring Sliding Interface

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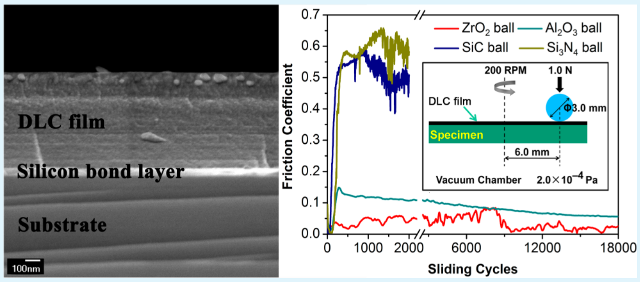
ABSTRACT: The high friction of diamondlike carbon (DLC) films in vacuum impedes achieving their application in space environment. Here we show that the vacuum friction coefficients can be lowered below 0.1 by avoiding formation of carbonaceous transfer layers on the counterfaces. First-principles calculations reveal that the low friction coefficients stem from intrinsically weak-interacting sliding interfaces. Conversely, formation of transfer layers and carbonaceous sliding interfaces thus established are invalid for friction reduction for DLC in vacuum. The mating materials are thus highlighted for their crucial roles in transfer-layer formation.



KEYWORDS: *diamondlike carbon, mating material, friction, high vacuum, first-principles calculation, adhesion*

INTRODUCTION

The lubrication of moving surfaces in a vacuum or space environment presents significant challenges to the researchers. Recently, amorphous hydrogenated carbon (*a*-C:H) has been examined as a potential solid lubricating material for space applications.[1,2] Heretofore, the typical polymerlike *a*-C:H (PLC) films with H content above a threshold of about 40 at.% are capable of yielding superlow friction (with friction coefficients below 0.01) and long wear life in high-vacuum.[2,3] However, incorporation of too much of H in the carbon matrix could deteriorate severely the tribological performance in humid air.[4] Given that the space mechanisms are also required to operate in air,[2] the PLC films probably are undesirable for space applications. As for the diamondlike carbon (DLC) films with relatively low H content, the friction coefficients fluctuate at high values (about 0.5 or even higher) in high-vacuum after a transient superlow friction regime.[3] Even so, the DLC films do exhibit excellent tribological properties in open air.[4] Hence, improving the vacuum performance of DLC films is imperative for the space applications.

In vacuum, the adhesion caused by interatomic forces between two contacted surfaces is the most common reason for the high friction and heavy surface damage.[5] Thus, the chemistry of the counterface material can be of critical importance for a given lubricating material such as the DLC film. However, the initial counterface materials were often quickly covered by carbon-rich transfer layers in vacuum as reported by most of the previous studies.[2,3,6] And the ultimate friction occurs between two carbonaceous surfaces which result in high friction and severe wear in high-vacuum due to the strong cross-interface carbon−carbon interactions in the case that the dangling bonds of carbon atoms at the interfaces are not sufficiently passivated.[3] Therefore, we propose an approach to achieve low friction and long durability for DLC films in high-vacuum: by avoiding the adhesive carbonaceous sliding interfaces. To test this hypothesis, SiC and Si_3N_4 with strong adhesion to carbon as well as Al_2O_3 and ZrO_2 with weak adhesion to carbon are chosen as mating materials. Two kinds of completely different tribological behaviors are obtained and discussed in terms of the ultimate sliding interfaces.

EXPERIMENTAL SECTION

The hydrogenated DLC film was deposited on silicon wafers and polished stainless steel substrates in a d.c.-pulse parallel-plate hollow-cathode system. To enhance the adhesion of DLC film, we first coated the substrates with a silicon bond layer. A mixture of CH_4 (100 sccm) and H_2 (200 sccm) gases was bled into the chamber to a working pressure of 50 Pa for film deposition. During deposition, the d.c. power was maintained at 72 W (voltage, −600 V; current, 0.40 A; pulse duty ratio, 30%) and pulse frequency was set as 1500 Hz. The deposition time was 360 min.

The fractured cross-section morphology and the thickness of the as-deposited film were examined using a JSM-6701F cold field scanning electron microscope (SEM). The hydrogen content of the as-prepared film was determined by time-of-flight elastic recoil detection analysis. The measurement was performed using 36 MeV iodine ions as incoming ion projectile. Raman spectroscopy with a laser excitation wavelength of 514.5 nm was employed to examine the structure characteristics of

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the as-deposited film. The mechanical properties (hardness and Young's modulus) were determined by a nanoindenter apparatus. The maximum indentation depth was limited to 10% of the film thickness to avoid substrate effects.

Besides, the friction tests were performed using a ball-on-disk apparatus in high-vacuum (2×10^{-4} Pa). The tested samples are DLC films deposited on polished stainless steel substrates. The SiC, Si_3N_4, Al_2O_3, and ZrO_2 balls of 3 mm in diameter with Ra ≤ 14 nm were used as the counterparts. All the tests were done at a sliding speed of 200 rpm, a rotational radius of 6 mm, and under a normal load of 1 N. The tests were stopped when the peak friction coefficient exceeded 0.3 after a minimum 2000 cycles or when a maximum of 18 000 cycles reached.

RESULTS AND DISCUSSION

Figure 1 shows (a) the SEM micrograph of fractured cross-section, (b) the fitted Raman spectrum, and (c) the nanoindentation load−displacement curve of the as-prepared film on a silicon wafer. As shown in Figure 2a, a film of 620 nm in thickness was deposited on a Si interlayer of 50 nm thickness. The hydrogen content is determined as about 8.03 at.% that is much lower than those of PLC films.[2−4] The Raman spectrum was fitted into two peaks with Gaussian line shape, with D peak centered at around 1360 cm^{-1} and G peak at around 1540 cm^{-1}, which is a typical characteristic of hydrogenated DLC films.[7] In addition, the as-prepared film possesses relatively high hardness and Young's modulus values of approximately 14.2 and 125 GPa, respectively, which further reveals the diamondlike feature of the film. Therefore, the studied film is identified as a low hydrogenated DLC film rather than a PLC film.

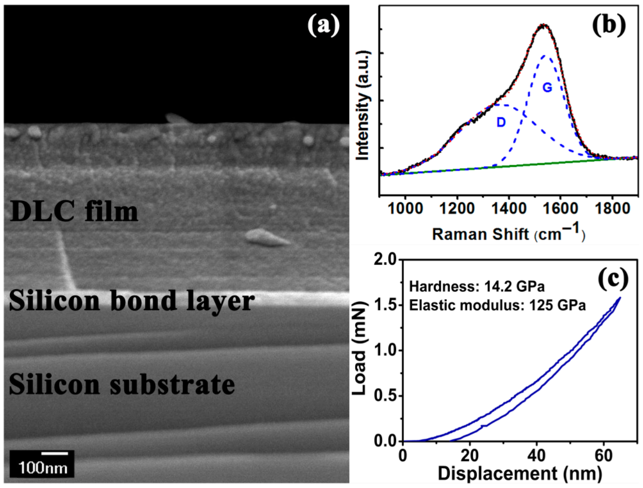

Figure 1. (a) SEM micrograph of fractured cross-section, (b) fitted Raman spectrum, and (c) nanoindentation load−displacement curve of the as-deposited DLC film.

Figure 2 shows the friction coefficient curves of DLC films against the four ceramic balls. On the basis of the characteristics of the curves, we divided them into two groups and display them in two panels. The first group includes the results obtained when SiC and Si_3N_4 balls were used as counterparts (Figure 2a); and the second group includes the curves derived from Al_2O_3/DLC and ZrO_2/DLC tribopairs (Figure 2b). The tribological behaviors of the DLC film against SiC and Si_3N_4 balls are similar to those of 'low hydrogenated AC8 film' against steel pin in ultrahigh vacuum as reported by Fontaine et al.,[3,8] which is consistent with the relatively low H content of the studied film. The friction coefficients increase rapidly to high values after a few tens of cycles of superlow friction (Figure 2a and the inset). Moreover, the film has been worn out after about 1000 cycles as indicated by the large fluctuations occurred (Figure 2a). In sliding against Al_2O_3 and ZrO_2 balls, surprisingly, the film exhibits low friction coefficients (the average friction coefficient for Al_2O_3 is 0.084 and for ZrO_2 is 0.037) and long durability (Figure 2b). The inset of Figure 2b shows 3D profiles of the two wear tracks after 18000 sliding cycles. The wear tracks have depth of about 150 nm for Al_2O_3 ball and 450 nm for ZrO_2 ball indicating the slight wear during the periods of sliding. It is unusual for DLC films in high vacuum to exhibit such low friction coefficients and wear rates.

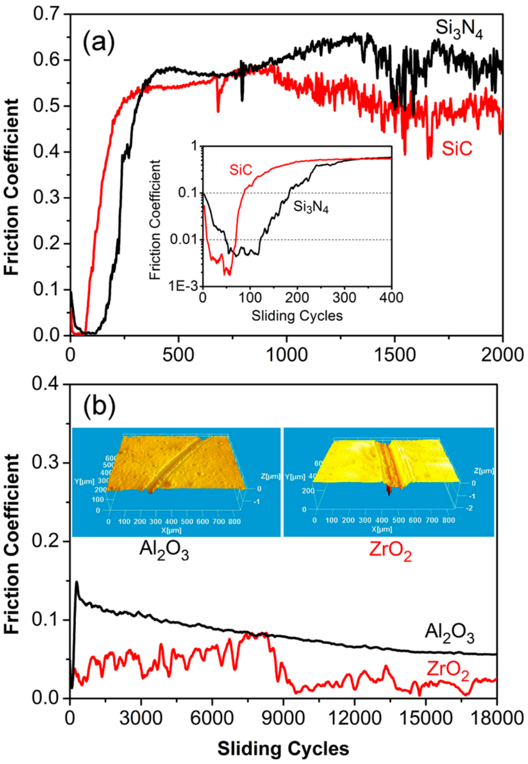

Figure 2. Friction coefficient curves of the DLC film sliding against different mating materials in high-vacuum (2×10^{-4} Pa): (a) SiC and Si_3N_4; (b) Al_2O_3 and ZrO_2. The inset of a shows the friction coefficient of the DLC film against SiC and Si_3N_4 balls in the initial 400 sliding cycles and the insets of (b) show 3D profiles of the two wear tracks on the DLC films after 18 000 cycles of sliding against Al_2O_3 and ZrO_2 balls.

The tribological behaviors of the DLC films largely depend on the chemical properties of the sliding interface. Conceivably, such low friction coefficients and wear rates displayed by the Al_2O_3/DLC and ZrO_2/DLC couples could have arisen from an unusual state of the sliding interface. Therefore, the wear surfaces on the counterparts were observed. The wear scars on SiC and Si_3N_4 balls were observed at a point when the friction coefficients reach a value of 0.3, where the film had not been worn out. As for the Al_2O_3 and ZrO_2 balls, the wear scars were observed after tests of 18 000 sliding cycles. The optical micrographs of wear scars on surface of the ceramic balls are shown in Figure 3. On the wear surfaces of SiC and Si_3N_4 balls, compact and black transfer layers are formed only after 150−250 sliding cycles (Figure 3a, b). However, no such transfer

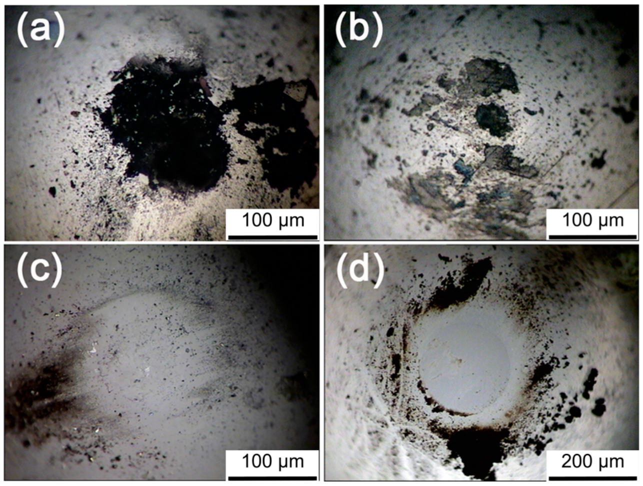

Figure 3. Optical micrographs of worn ball surfaces: (a) SiC, (b) Si_3N_4, (c) Al_2O_3, and (d) ZrO_2.

layers are observable on the wear scars of Al_2O_3 and ZrO_2 balls even after 18000 cycles (Figure 3c, d). Similar results were reported by Liu et al.,[9] where no carbonaceous transfer film was formed on the wear scar surface of Al_2O_3 ball after 2 h of sliding test in room air against DLC film, whereas on SiC and Si_3N_4 wear surfaces, black transfer layers were formed. Erdemir et al.[10] also claimed that oxide-based ceramics such as Al_2O_3 and ZrO_2 have poor tendency to form carbonaceous transfer layers on their sliding surfaces. However, formation of carbonaceous transfer layers gives rise to high rather than low friction for the DLC film in high-vacuum. It is contradictory to the concept of transfer layers leading to low friction[3,6,11] and has to be elucidated.

The significantly distinct of transfer-layer formation points to the probable difference among adhesions of the counterface materials to carbon. Determining the adhesion of the ceramics/carbon interfaces will also contribute to clarifying the impacts of mating materials on the vacuum tribological properties of DLC films. First-principles calculations of work of separation (W_{sep}) provide a useful and convenient measure of the interface adhesion strength. Hence, we use first-principles calculations to study adhesion between ceramic mating materials and carbon with aim to gain more fundamental understanding of the frictional mechanism of DLC films in vacuum.

The first-principles calculations were carried out using CASTEP code,[12] which uses the energy plane-wave pseudopotential total calculation method based on the density functional theory. The generalized-gradient approximation with the Perdew−Burke−Ernzerhof exchange-correlation functional is chosen for all the calculations. A plane-wave cutoff energy of 340 eV and Monkhorst−Pack *k*-point meshes with a density of $(6 \times 6 \times 1)$ were employed throughout. The energy tolerance was 1.0×10^{-5} eV/atom, the force tolerance was 0.03 eV/Å, and the displacement tolerance was 0.001 Å. The calculated values were obtained at 0 K. To minimize the mismatch between constituent slabs and meanwhile achieve smallest interface areas, specific crystal forms and crystal faces were chosen to construct interfaces which are illustrated in Figure 4. Because the C−H bonds at the sliding interface will break readily during friction process especially under high-vacuum conditions,[13] the tribological surface of DLC film is represented by a diamond surface such as (111) or (100).[14] The W_{sep} can be computed via

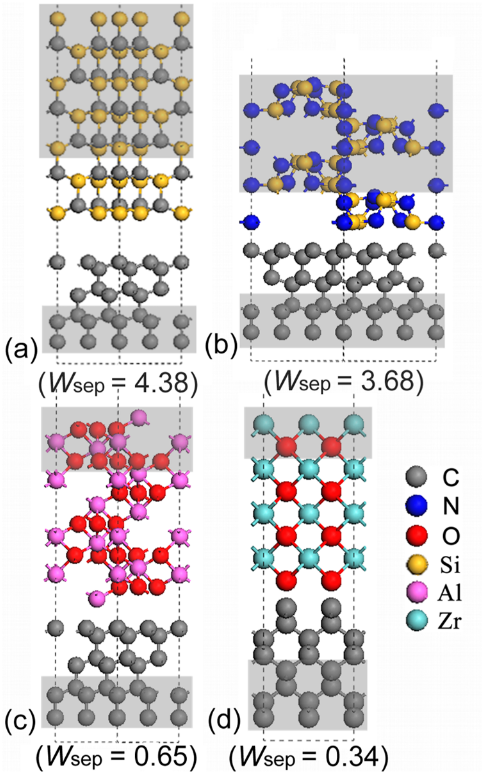

Figure 4. Interface structure of (a) SiC(001)/diamond(111), (b) Si_3N_4(001)/diamond(111), (c) Al_2O_3(001)/diamond(111), and (d) ZrO_2(001)/diamond(001). Space groups for SiC, Si_3N_4, Al_2O_3, and ZrO_2 are $P6_3mc$, $P6_3/m$, $R\bar{3}c$, and $Fm\bar{3}m$, respectively. The parts in shadow are fixed to represent bulks of the slabs and the other parts are allowed to relax. W_{sep} values in J/m^2 are shown in the parentheses below the respective structures.

$$W_{sep} = (E_1^{tot} + E_2^{tot} - E_{12}^{tot})/A \qquad (1)$$

where E_1^{tot} and E_2^{tot} are the total energies of the slabs 1 and 2, E_{12}^{tot} is the total energy of the interface system with slabs 1 and 2, and A represents the interface area. The $E_1^{tot} + E_2^{tot}$ values were calculated by relaxing the atomic coordinates of the two constituent slabs with a separation of 15 Å and the E_{12}^{tot} values were obtained by relaxing the interface structures with a proper separation. The W_{sep} values are shown in Figure 4 as well. The large W_{sep} values for SiC/diamond (4.38 J/m^2) and Si_3N_4/diamond (3.68 J/m^2) couples indicate that there should be strong chemical bonds between the interface SiC (Si_3N_4) and carbon.[15] However, the interfaces of Al_2O_3/diamond and ZrO_2/diamond exhibit small W_{sep} values (0.65 and 0.34 J/m^2, respectively), which implies weak interactions between Al_2O_3 (ZrO_2) and carbon at the interface. Distributions of electron density further reveal the difference in adhesions between diamond and the four ceramics (Figure 5). There is markedly overlapping of electron density for SiC(001)/diamond(111), but there is no almost electron density for Al_2O_3(001)/diamond(111) in the interface region. In addition, these W_{sep} values are qualitatively consistent with the measured adhesion of DLC films to smooth ceramic substrates as reported by Erck et al.[16] They found that excellent adhesion was measured for smooth SiC and Si_3N_4, whereas adhesion of DLC to smooth Al_2O_3 and ZrO_2 was vanishingly small.[16]

On the basis of the experimental results and first-principles calculations, one can conclude that the adhesion between

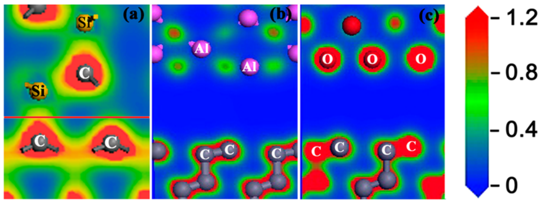

Figure 5. Distributions of electron density of optimized (a) SiC(001)/diamond(111) and Al_2O_3(001)/diamond(111): the slice across (b) Al atoms and (c) O atoms. There are 128 contour levels plotted with blue corresponding to 0 and red to 1.2 e/Å^3, as indicated in the scale bar.

mating material and carbon determines to a great extent the ultimate frictional interface. If the mating material is of strong adhesion to carbon (i.e., with large W_{sep} value in the present study), the loose carbon species of DLC will migrate to the counterface and form carbonaceous transfer layers. In this case, the sliding will take place between two carbonaceous surfaces. Conversely, if the mating material is of weak interaction with carbon, carbonaceous transfer layers may not be formed and the steady-state sliding will occur between the "parent" materials of the sliding couple.

In vacuum, owing to the negligible effects of environmental species, the intrinsic properties of the sliding interface play a decisive role in the friction and wear process. The formation of carbonaceous transfer layers on the counterface and thus carbonaceous sliding interface established are usually recommended to interpret the low friction of carbon-based materials in air[11,17] and the superlow friction of PLC in high-vacuum.[3] The underlying prerequisite is that the dangling bonds of carbon atoms at sliding interface must be sufficiently passivated.[18] In air or other environment where chemically active molecules such as water and oxygen are abundant, the carbon atoms can be passivated by these extrinsic species.[19] In high-vacuum, the PLC film achieves sufficient passivation by the plenty of hydrogen that resides in the bulk of the film.[3,8] As for the DLC film, unfortunately, the H content is low; therefore, only transient sufficient passivation can be fulfilled by the exodiffusion of "free" hydrogen that embedded in the bulk of the film to terminate the exposed dangling bonds of carbon atoms.[8] Once the "free" hydrogen is depleted, the strong carbon−carbon interactions across the sliding interfaces will inevitably occur and will lead to high friction and severe wear.[8] Consequently, formation of carbonaceous transfer film on the counterface is not effective, may be harmful,[20] for reduction of friction and wear in high-vacuum for the DLC films.[20,21] Conversely, in sliding with mating materials that are of weak interactions with carbon such as Al_2O_3 and ZrO_2, the transfer films are not formed; thus the strong carbon−carbon interactions can be avoided. Thanks to the intrinsically weak-interacting sliding interface, the DLC film is capable of yielding low friction and long wear life in high vacuum. The discussion above also explains results observed in dry air by Klaffke.[22]

In addition, we must state here that although we highlight the pivotal roles of mating materials, we do not mean to undermine the importance of hydrogen. Voevodin et al.[21] demonstrated that the non-hydrogenated DLC film displayed high friction coefficient (∼0.5) when tested against Al_2O_3 in high-vacuum with carbonaceous transfer film formed on the counterface. Hydrogen can only act as a terminal atom to deactivate the dangling bonds of carbon atoms; therefore, the existence of hydrogen further weakens the adhesion of carbon to the counterface material[15] and thereby inhibits the formation of transfer layers[23] that cause high friction and severe wear.

New design possibilities are offered by doping with other elements to further optimize the tribological performance of DLC against Al_2O_3 or ZrO_2 in high vacuum. We consider sulfur as one of such elements, because repulsions between S atoms and O^{2-} ions in Al_2O_3 has been discovered by Marino et al.[24]

■ CONCLUSION

We show that the adhesion between mating materials and carbon can greatly affect the vacuum tribological behaviors of DLC films. Converting the conventional but intrinsically adhesive carbonaceous sliding interface into a weak-interacted one, and thereby improving the DLC's vacuum tribological performance can be realized by sliding against materials with low adhesion to carbon to avoid formation of carbonaceous transfer films. We ascribe the low friction of DLC/Al_2O_3 and DLC/ZrO_2 tribopairs in vacuum to the intrinsically weak interactions between two sliding materials. This simple route to achieve low friction and long wear life for DLC films in high vacuum is desirable for space applications.

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Notes

The authors declare no competing financial interest.

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