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Perspectives to friction mechanism of a-C:H film in vacuum concerning onion-like carbon transformation at sliding interface

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Abstract: a-C:H films with low friction and good wear resistance have long been regarded as a potential space lubricating film. However, its superlubricity mechanism and failure process in vacuum still remain to be improved. To clarify its friction mechanism, here we systematically investigated tribological property of a typical a-C:H film under high vacuum environment. The results show that the extremely low friction coefficient last 2700 cycles under contact pressure of 930 MPa, and the whole friction process can be divided into three stages. The friction coefficient firstly kept a stable and low value after a short period of running-in, then it underwent an obvious fluctuation period and further decreased to an extremely low value (0.005) until abrupt failure. The structural evolution of a-C:H film on the sliding interface in

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different periods through the whole friction process was characterized and a dynamic friction mechanism is established. The self-mated (a-C:H/a-C:H) friction process and hydrogen passivation contributed to decrease the friction coefficient at the early stage of sliding. Then, the emission of hydrogen became evident under high local stress and more dangling bonds were exposed on the worn surface, which leads to the wild adhesion wear between the sliding surfaces. The alternated process between old film and new film is in consonance with the fluctuation of friction coefficient. Afterwards, carbon onions with a closed spherical shell structure are spontaneously formed on the worn surface in the absence of hydrogen passivation effect, which further reduce friction coefficient to an extremely low value. This study provides guidance to further designing of a new generation of a-C:H film with a special structure that exhibits a better tribological performance in vacuum environment.

Key words: a-C:H film; high vacuum; carbon onion; friction and wear mechanism

1. Introduction

Along with the increasing demand of humankind for space exploration, the development of high-performance solid lubricants as well as solid lubrication technology applicable to long-term operation of mechanical assemblies in vacuum environment is becoming increasingly urgent. However, the space environment, involving ionizing radiation, atomic oxygen, weightlessness, and sharp temperature change, is very complicated and brings about challenges to traditional solid lubrication films [1]. Hydrogenated diamond-like carbon (a-C:H) films with low friction and good wear resistance, excellent biocompatibility, high hardness and

electrical resistivity, as well as high chemical inertness have been widely referenced

as a potential space lubricating material [2-4]. Unfortunately, lifetime of a-C:H films

for preserving the superlow friction regime in vacuum environment is still not very

satisfactory [5-7]. So far, a large number of attempts have been successfully made to

explore friction and failure mechanism of a-C:H film in vacuum [8-11]. Hydrogen

passivation and emission mechanisms were found to exert a great influence on

tribology performance of a-C:H film in vacuum. When hydrogen content in the film

increases to a certain value (34%∼40%), the extremely low friction coefficient can be

maintained for a longer time[9]. In addition, adding a certain amount of hydrogen

during friction tests also helps to prolong the life span of a-C:H film in vacuum

environment. As a-C:H film is a three-dimensional covalent structure constructed of

sp^2 and sp^3 hybridized carbon atoms, chemical bonds in the film will be broken by the

repeated friction process and large amounts of dangling bonds will be exposed on the

worn surface, which cause strong chemical interactions on rubbed surfaces that results

in a high film friction coefficient and rapid failure. If more hydrogen atoms exist in

film or environment, the dangling bonds can be well passivated and a low friction

coefficient can be maintained [12]. However, many researches also indicate that the

wear life of a-C:H film in vacuum do not just depends on hydrogen content. For

example, NFC-6 amorphous carbon film (the content of hydrogen is about 40%) that

was prepared by Erdemir et al. [13, 14] exhibited a super low friction coefficient

(about 0.001) in dry nitrogen atmosphere, while the lubrication ability of the film only

remained dozens of cycles in vacuum environment. Vanhulsel et al. [15] also reported

that the wear life of a-C:H film with a hydrogen content of 51% is shorter than that with 49% hydrogen in vacuum environment. In addition, Chen et al. [16-17] reported that the life of a-C:H film was closely related with internal stress. Fontaine et al. [18] claimed that the viscoplasticity also significantly influenced the wear life of the film. Liu [2] prepared a novel hydrogenated amorphous carbon film with a self-organized dual nanostructure exhibited a super-high elastic recovery of 95% and excellent tribological properties under vacuum. These phenomena indicate that friction and wear process of a-C:H film in vacuum is a very complex process and it is greatly influenced by many factors. A more in-depth study needs to be conducted to investigate the friction behavior of a-C:H film in vacuum, which can provide guidance for developing a new generation of a-C:H film with a longer life in vacuum.

Based on these previous studies, in the present research, the failure process of a typical a-C:H film with extremely low friction coefficient in vacuum was investigated. In view of the fluctuation of friction coefficient, the morphology and structure of worn surface in different periods were characterized respectively, in order to establish a dynamic friction mechanism of a-C:H film throughout the whole friction process.

2 Experimental details

2.1 Preparation of a-C:H films

The a-C:H films were deposited on polished stainless steel substrates (1Cr18Ni9Ti; φ24 mm × 8 mm, 220HV) and silicon wafer substrate with a medium frequency unbalanced magnetron sputtering facility (SP-0806SI). The details about the deposition facility and deposition process were described elsewhere [17]. At first,

the Si interlayer was deposited on the substrates in advance for about 280 nm to increase the adhesion strength between the a-C:H films and substrate. During the carbon film sputtering process, the deposition time was fixed at 3.5 h, and a-C:H film is about 1.4~1.5 um thick.

2.2 Characterization of a-C:H films

The fractured cross-section morphology of as-prepared film was observed by a JSM-6701F field emission scanning electron microscopy (FESEM). JEOL-2010 high-resolution transmission electron microscopy (TEM) was used to observe the microstructure of as-prepared film. The Jobin-Yvon HR-800 Raman spectrometer with an Ar^+ laser of 532 nm line was used to characterize the detailed bonding structures of the film as well as worn surfaces. The nano hardness of a-C:H films was evaluated using a Nanotest600 nanoindenter apparatus (Micro Materials Ltd., UK) with a Berkovich indenter at a load of 5 mN. The maximum indentation depth was less than 10% of the film thickness to minimize the substrate contribution.

2.3 The exploration on vacuum tribological behavior

Vacuum friction and wear tests were conducted with a rotational ball-on-disk tribometer that was sealed in a vacuum chamber. The details about this apparatus were described elsewhere [19]. Friction tests of GCr15 steel ball (radius: 6 mm) against a-C:H film were conducted at a normal load of 5 N (corresponding maximum contact stress is about 930 MPa), a pressure of 1.0×10^{-4} Pa, a sliding speed of 0.18 m/s. It was assumed that the tested a-C:H films failed when the value of friction coefficient exceeds 0.15. Friction experiments were conducted at least three times under same

experimental conditions. Then, the tribological performance of the film after different

test durations was investigated. The test duration was selected as 300 cycles, 700

cycles, 1000 cycles and 2400 cycles respectively. After friction and wear tests, the

morphology of worn surfaces was observed by SEM and non-contact three

dimensional surface profilometer (ADE Corporation, Massachusetts, USA). The

structural information and phase compositions of worn surfaces of both the film and

corresponding steel counterface were characterized by TEM and Raman spectrometer.

3. Results and discussion

3.1 General properties of as-prepared a-C:H film

Figure 1 shows the FESEM and TEM morphologies of as-prepared a-C:H film.

As seen from Figure 1a, the film shows a dense microstructure and well adheres to Si

wafer substrate. The total thickness of the film is about 1.716 μm including a 1.435

μm of a-C:H film and a 0.281 μm of pure silicon interlayer. According to TEM image

and corresponding electron diffraction pattern in Figure 1b, it can be found that the

a-C:H film exhibits amorphous structure. In addition, the as-deposited film possesses

a relatively high hardness of 9.17 GPa and Young's modulus of 66.14 GPa.

3.2 Friction and wear behavior of as-prepared a-C:H film in high vacuum environment

The friction coefficient curves of a-C:H film under vacuum environment are

shown in Figure 2. It clearly reveals that friction test results are fairly reproducibility.

The variation of the friction coefficient with sliding cycles can be approximately

divided into three stages. Namely, at the initial stage, the friction coefficient sharply

declines to a stable low value (0.01) after a short period of running-in and remains

stable up to about 350 cycles. Then it undergoes obvious fluctuation period in sliding

cycles of 350~750. At the third stage (referring to sliding cycles of 750~2600), the

friction coefficient is further decreased to an extremely low value (0.005) and tends to

be stabilized thereat, followed by an abrupt rise above a sliding cycles of 2700 cycles

at which the failure of the a-C:H film starts. In addition, this similar variation of

friction coefficient has been reported in those previous reports [16-17, 20-21],

however, a detailed research on this peculiar friction phenomenon has never been

reported.

3.3 SEM observation of worn surfaces of a-C:H film and steel ball counterface

To acquire more insights into the correlation between the friction behavior of

a-C:H film and sliding cycles, we conducted friction tests at durations of 300 cycles in

the initial stable period, 700 cycles corresponding to the evident fluctuation period,

1000 cycles at superlow friction stage after fluctuation period, as well as 2400 cycles

that approach to failure. Corresponding SEM images of worn surfaces of a-C:H film

as well as steel ball counterface after different friction durations are shown from

Figure 3 to Figure 6.

It can be seen that the wear scar of a-C:H film after 300 cycles of sliding is

shallow and smooth without any obvious signs of damage (Figure 3a), which

indicates that the film underwent very slight wear at the early stage of friction.

Besides, a continuous and thin transfer layer seems to have formed on the surface of

the counterface steel ball (Figure. 3b) in this case, which well corresponds to the low

and stable friction coefficient therewith.

When the sliding cycles is extended to 700 cycles, obvious sign of scuffing in association with a few wear debris is visible on the worn surface of a-C:H film. Some sub-layer films seem to have been newly exposed on the wear scar owing to mild adhesion wear (Figure 4a and b), while an increased amount of film materials seem to be detached and transferred onto the worn surface of the counterface steel (Figure 4c). These observations well correspond to the obvious fluctuation of the friction coefficient in the sliding duration of 350~750 cycles.

As the sliding process further increases to 1000 cycles, corresponding worn surface of a-C:H film shows signs of severe adhesion and scuffing as well as obvious spalling in association with an increased amount of wear debris (Figure 5a and b), while more film materials seem to have been transferred onto the worn surface of the steel counterface, but no compact and continuous transfer film is formed on the sliding surface (Figure 5c). Such worn surface features seem to be contradictory to the very low and stable friction coefficient in the sliding cycles range of 750~1000, and the reasons accounting for this phenomenon will be further discussed in the following section.

When the sliding cycle reaches 2400 cycles, it seems that the worn surface of a-C:H film is covered by a certain material (Fig. 6a and b). The spalling and scuffed grooves become more prominent after the worn film surface is ultrasonically cleaned (Figure 6c). In the meantime, as seen in Figure 6d, wear track of the steel ball is notably enlarged and covered by a discontinuous transfer film. This is seemingly also

contradictory to the quite low and stable friction coefficient in this period.

3.4 Three-dimensional morphology analysis of worn surface of a-C:H film

The non-contact 3D surface morphologies of the a-C:H film after sliding against the steel counterface at different cycles are shown in Figure 7. It can be seen that both the width and depth of the wear scar increase with extending sliding cycles. After 300 cycles of sliding, the wear scar of the a-C:H film is shallow and shows few signs of plough grooves with a wear depth of about 630 nm (Figure 7a), while 700 cycles of sliding gives rise to a deeper (900 nm in depth) and wider wear scar dominated by mild adhesion and scuffing (Figure 7 b). As the sliding cycles further rise to 1000 cycles and 2400 cycles, the wear scar of the a-C:H film is further widened and more severe adhesion and scuffing are observed (Fig 7c and d).

3.5 Raman spectrometric analysis of worn surface of a-C:H film and counterface steel ball

Figure 8 shows Raman spectra of as-prepared film and worn surfaces of a-C:H film after sliding at different cycles. All of the worn surfaces of a-C:H film in different durations show a sharp G peak at about 1550 cm^{-1} and a D peak at about 1380 cm^{-1} (Figure 8), which is consistent with the typical structure feature of diamond-like carbon coatings [22]. Interestingly, along with the increase of the sliding cycles, the G peaks of the worn surfaces of a-C:H film tend to gradually shift towards higher frequency region, while the intensity of the D peaks tends to rise therewith (Table 1). This implies that extending sliding cycles helps to enhance the structural change of film on the frictional interface [23-24], which is related to the

variation of friction coefficient at extended sliding cycles of 750 cycles and above.

3.6 TEM analyses of worn surfaces of a-C:H film at sliding cycles of 700, 1000 and 2400

As what is reported elsewhere, extending of sliding cycles causes severe adhesion wear on the sliding surface, thereby finally leading to the failure of a-C:H film [25-26]. In the present research, severe adhesion wear, scuffing and even film peeling off are also observed when the sliding cycles are extended to 1000 cycles and 2400 cycles, but the friction coefficient is lowered to a very low level (about 0.005) and stabilized there after an obvious fluctuation in the sliding cycles range of 350~750. To reveal possible reasons leading to such an anomalous change of the friction coefficient of the a-C:H film, we conducted TEM analyses of the worn surfaces of a-C:H film after sliding cycles of 700, 1000 and 2400. TEM images of the worn surface after sliding for 700 cycles are displayed in Figure 9a and b. Some regular particles at the nanoscale are clearly visible on the worn surface after 700 cycles (Figure 9a). Moreover, the magnified TEM image in Figure 9b further reveals that these particles mainly show an amorphous structure that is very similar to the original film. However, some lamellar structures have been formed at the edge of these particles and the distance between the planes is approximately 0.34 nm that closely matched the lattice parameter d_{002} of bulk graphite [27]. After sliding for 1000 cycles, it is worth noting that some highly ordered spherical nanoparticles with a size of 25~35 nm emerge on the frictional interface of a-C:H film (Figure 9c). The magnified image in Figure 9d further indicates that the ordered spherical

nanoparticles consist of onion-like carbon which comprise of concentric graphitic shells [28] and the distance between the graphite shells is also approximately 0.34 nm. When the sliding cycles reaches 2400, similar spherical nanoparticles are also remained on the wear scar (Figure 9e). Nevertheless, as shown in Figure 9f, the integrity of the onion-like carbon structure after 2400 cycles is destroyed to some extend and especially its outer layers are peeled off obviously, which is possibly damaged by repeated shear force at adequately extended sliding cycles. Therefore, we suppose that the graphite nanosheets consisting of onion-like carbon, generated via increased sp^2 bond at extended sliding cycles, accounts for the extremely low friction coefficient of a-C:H film at extended sliding cycles of 1000 and above (up to about 2400 cycles).

3.7 Friction mechanism of a-C:H film in vacuum environment

According to the above-mentioned analyses, a dynamic friction mechanism of a-C:H film in different friction period under vacuum environment can be schematically illustrated in Figure 10. As shown in Figure 10a, at the first stage (within 300 cycles), the initial contacts mainly occur between a-C:H film and steel ball. During this process, repetitive sliding between the two contact surfaces leads to transfer of the film material onto the steel ball counterface thereby generating a continuous ultrathin transfer film thereon at the early stage of sliding. Along with the formation of the continuous transfer film, the original film-steel contact is transformed to a-C:H film /a-C:H film contact. As a result, the friction coefficient is significantly reduced owing to strong hydrogen-passivation between the sliding

interfaces [29-30].

As the friction process increases to 700 cycles (Figure 10b), local hydrogen bonding of the a-C:H film is partly destroyed under long-time repeated shear force [31], thereby exposing active bond at the contact interface where mild adhesion wear occurs and then the local weld zone is sheared off [25]. In addition, as we all known, a-C:H films are very brittle and process the high internal stress, so the wear debris are easily produced during the adhesive process. At the same time, the friction coefficient began to be a little higher and instable. As a result, the adhesion process as well as the alternate appearance of worn film and fresh film leads to the obvious fluctuation of friction coefficient therewith [32].

Following the fluctuation process, though more severe adhesion wear and then local weld zone is sheared off at further extended sliding cycles (Figure 10c), the friction coefficient is even lowered to an extremely low level (0.005), which is due to the formation of well-ordered onion-like carbon structure on the sliding surface (Figure 10d). The formation of such a special carbon structure on the frictional interface should involve complex factors, such as mechanical excitation, frictional heating, and even polymerization and oxidation [32]. In brief, the constant breaking of hydrogen bonding on the worn surface leads to the generation of two-dimensional graphite nanosheets that can further transform into onion-like carbon structure [33]. Bollmann et al. reported that a rolling up of graphite nanosheets at the tribological interface can act like a roller bearing that not only decreases surface energy but also forms the superlubricity friction interface [34]. Thus, we can reasonably infer that it is

the onion-like carbon structure on the sliding surface that accounts for significantly reduced friction coefficient at extended sliding cycles. On the one hand, the onion-like carbon nanoparticles can serve as spacers to prevent the direct rough contact between the rubbed surfaces. On the other hand, onion-like carbon structures could act as nano-scale ball bearings to transform the sliding friction to rolling friction to some extent, thereby contributing to reduced friction. In addition, there are no dangling bonds at the surface of the onion-like carbon structure subjected to ordering under an extended sliding cycles of 1000 cycles, and hence weak intermolecular bonding with the counterface material might also account for reduced friction coefficient to some extent [35].

However, when the sliding cycles is further extended to a high enough level, the onion-like carbon structure will be gradually exfoliated and destroyed in the contact area under the repeated shear force. Namely, the outer layers of the onion-like carbon structure will be peeled off to generate many graphite fragments. As a result, the direct contact between the counterface steel ball and the graphite fragments leads to the rapid deterioration of wear condition in association with the abrupt rise of the friction coefficient and ultimate failure of the a-C:H film.

4 Conclusions

The friction and wear behavior of as-prepared a-C:H film on the stainless steel substrate were evaluated in vacuum environment, and the correlation between the tribological behavior of a-C:H film and the sliding cycles was systematically investigated. A dynamic friction mechanism of a-C:H film throughout the whole

friction process is successfully established. It is worth noting that carbon onions with a closed spherical shell structure were spontaneously formed on the worn surface in the absence of hydrogen passivation effect, which further reduced friction coefficient of the film to an extremely low value. This study would provide guidance to further designing of a new generation of a-C:H film with a special structure that exhibits a better tribological performance in vacuum environment.

Acknowledgments

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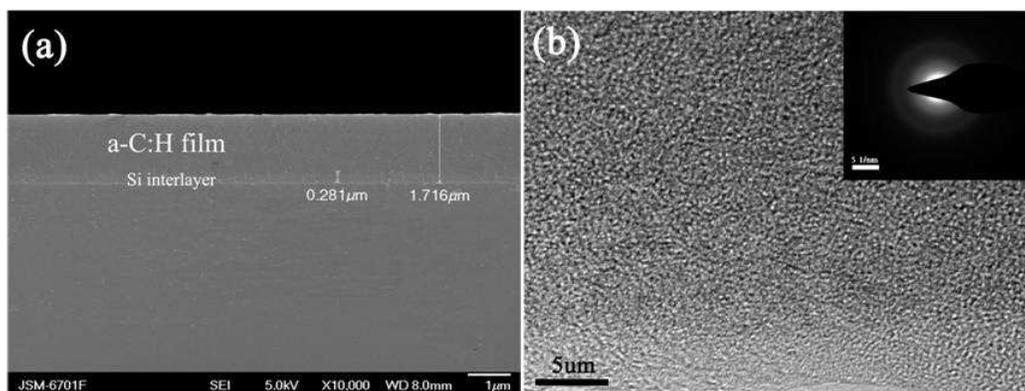
Figure 1. FESEM image of fractured cross-section (a) and TEM micrograph (b) of

as-prepared a-C:H film
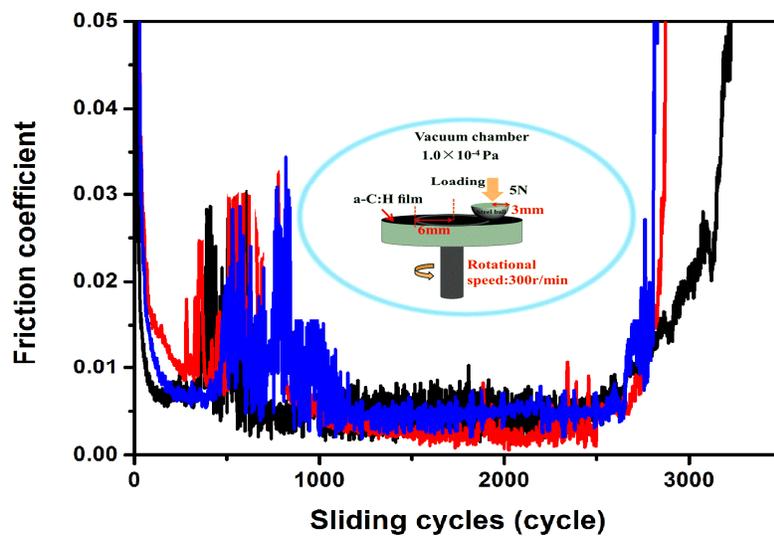
Figure 2. Friction coefficient curves of a-C:H film under vacuum environment.
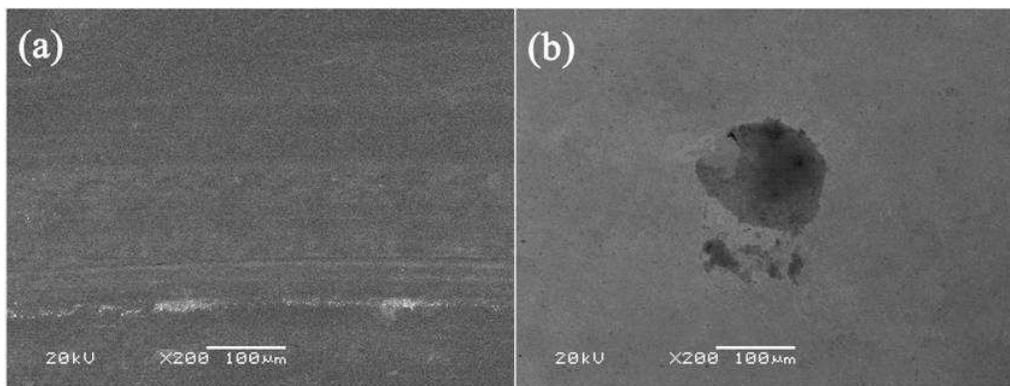
Figure 3. SEM images of worn surfaces of a-C:H film (a) and steel ball counterface

(b) after 300 cycles
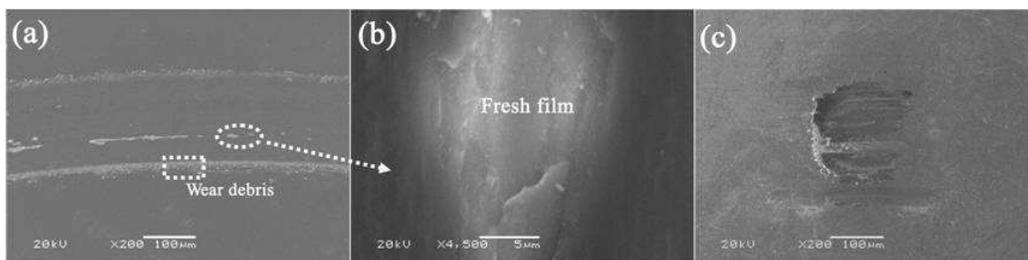
Figure 4. SEM images of worn surfaces of a-C:H film (a, b) and steel ball

counterface (c) after 700 cycles

Figure 5. SEM images of worn surfaces of a-C:H film (a, b) and steel ball

counterface (c) after 1000 cycles
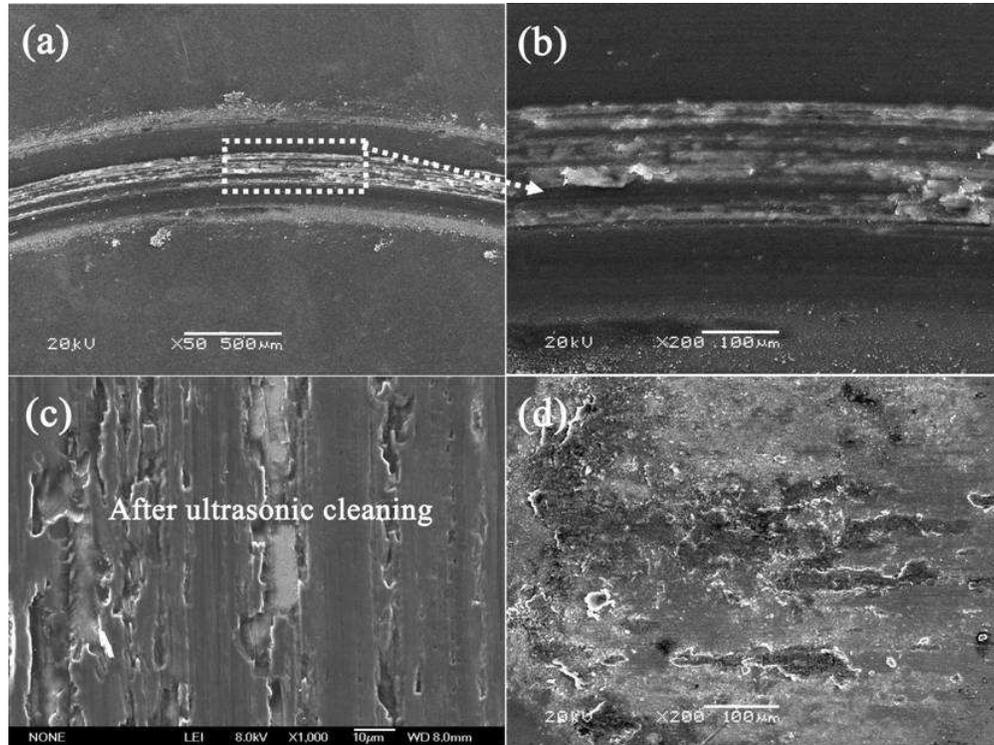
Figure 6. SEM images of worn surfaces of a-C:H film (a-c) and steel ball counterface

(d) after 2400 cycles
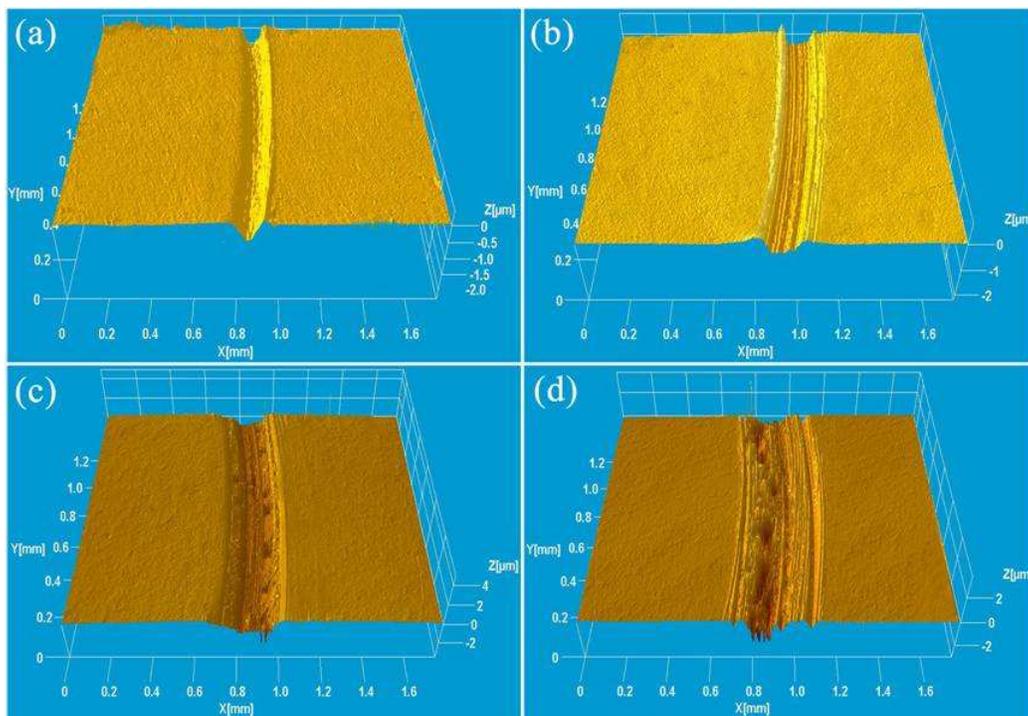
Figure 7. Three-dimensional surface morphologies of a-C:H film after sliding against

steel counterface at 300 cycles (a), 700 cycles (b), 1000 cycles (c),

and 2400 cycles (d).
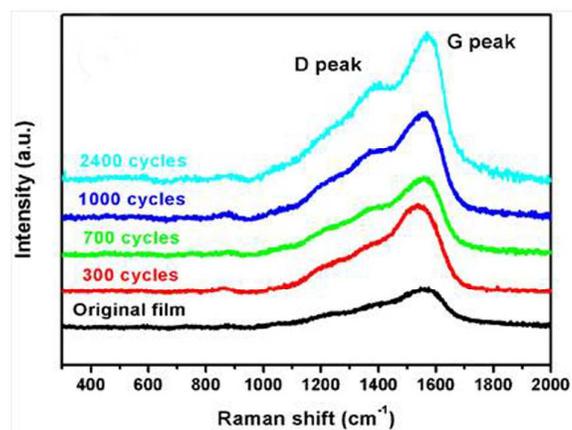
Figure 8. Raman spectra of as-prepared a-C:H film and worn surfaces of a-C:H film

after different sliding cycles
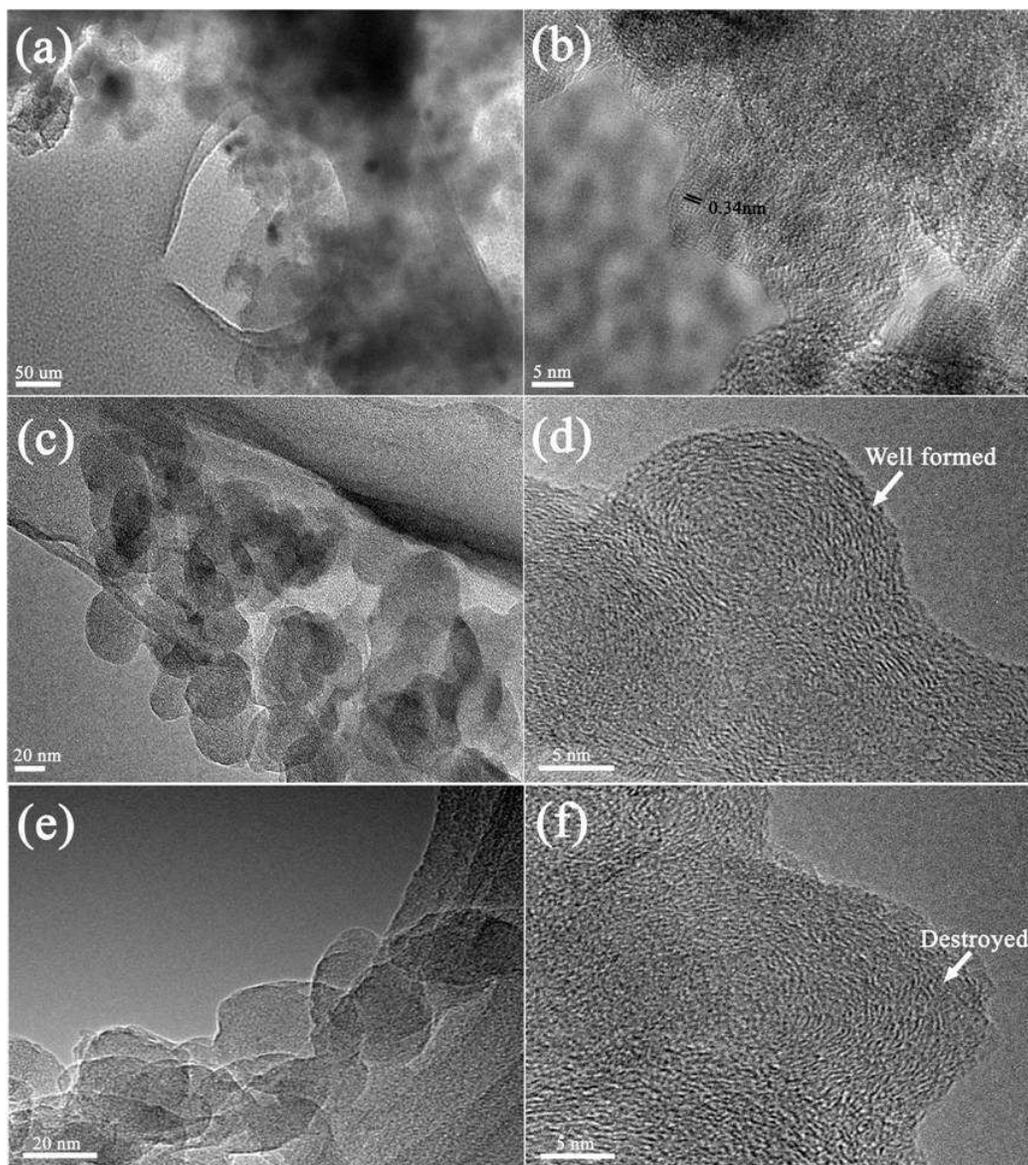
Figure 9. TEM images of worn surfaces of a-C:H film after sliding against the steel

ball counterface after 700 cycles (a, b), 1000 cycles (c, d) and 2400 cycles (e, f)
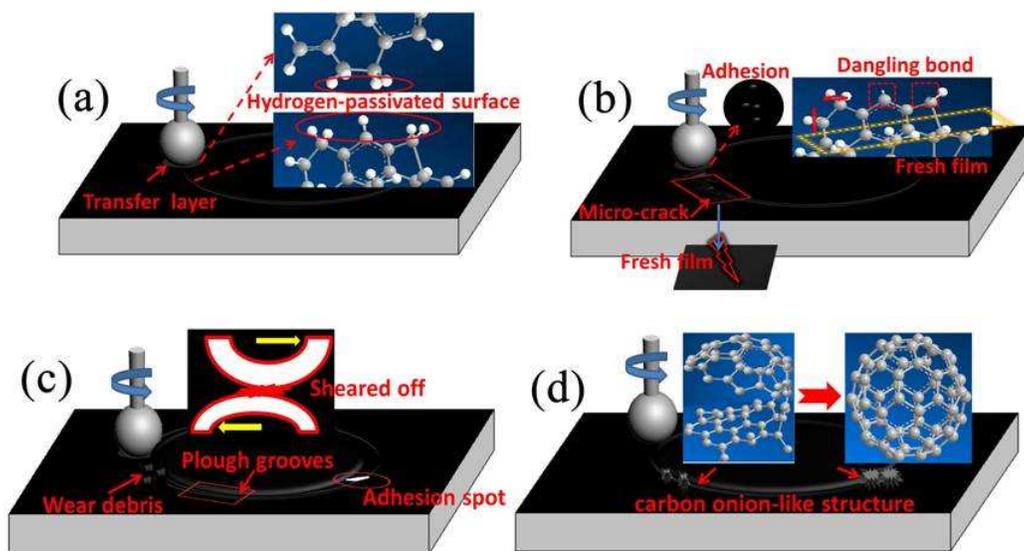
Figure 10. Schematic diagram illustrating the friction and wear process of a-C:H film

in vacuum environment

Table1 the fitting results of Raman spectra in Fig. 8

Investigated spot	D peak position(cm^{-1})	Gpeak position (cm^{-1})	ID/IG
Original film	1364.4	1531.9	1.75
after 300 cycles	1368.3	1536.1	1.8
after 700 cycles	1377.8	1545.6	1.92
after 1000 cycles	1392.1	1555.6	2.02
after 2400 cycles	1406.0	1557.1	2.43