Fullerene-Like Structure Hydrogenated Carbon Film: One Way to the Industrial Scale Supelubricity

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Book Chapter

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Abstract

Fullerene-like structure hydrogenated carbon films, one of the solid lubricants that can realize macroscopic superlubricity, can be used in engine parts for fuel economy, like common rail, valve tappet. Usually, superlubricity refers to slide friction coefficient of about 0.001 range or below, which can sufficiently help reducing friction and wear lost, i.e. mechanical systems with utilizing of superlubricity performance are imperative to save energy and to reduce hazardous waste emissions into environment. Hitherto, superlubricity has been captured in experiments performed using the graphene, molybdenum disulphide (MoS_2), and hydrogenated carbon films, etc. However, superlubricity phenomenon may diminish under engineering scale of these structures. In order to overcome the drawback, designing and drawing the formation of graphene nanoscrolls at friction interfaces between fullerene-like carbon films and counterparts can achieve superlubricity at open atmosphere. Therefore, this chapter take fullerene-like carbon films, which hold superlubricity properties, as the object of discussion. In a word, the chapter are mainly describing film growth methods as well as growth mechanism, depicting the factors influencing on film structure and exhibiting the friction and wear properties. At last, some of industrial application examples are exhibited, and the potential challenge for future works are proposed in a short summary.

Introduction

Friction is a universal phenomenon which exists from atomic scale to cosmic scale, such as walking, earthquake, typhoon, and even galaxy collisions. For the adverse results caused by friction,

there has been significant effort to reduce the friction through improved lubricants, engineered surfaces, optimized mechanical systems and so on [1-2]. Generally, the effectiveness of improving friction performance is evaluated by the friction coefficient values. T. Spalvins firstly classified the scope of friction coefficient into ultralow friction (0.01-0.04) and superlow friction (<0.01) [3]. In present, considering the users habit, it is classified into low friction (~0.1), ultra-low friction (~0.01) and super-low friction (~0.001). The most interesting phenomenon is super-low friction, also named superlow-, superlubric-, superlubricious- as well as superlibricant- friction, but bearing a proud name of "superlubricity" [4-7]. Superlubricity, a most beautiful word on tribologists' lips, has been defined by Hirano and Shinjo [8,9]. However, superlubricity refers to slide friction coefficient about ～0.001 range or below, which can help reducing the friction and wear lost. In a word, developing superlubricity technology can not only save energy but also reduce hazardous waste emissions into environment [2].

In the past decades, many efforts were attributed to build superlubricious system and revealed the nature of superlubricity mechanism [10-14]. The most discussed materials with superlubric properties are carbon-based ones, like graphene, graphite, carbon nanotube, hydrogenated diamond-like carbon (DLC) films, nanodiamond films and fullerene-like hydrogenated carbon (FL-C:H) films [11,12,14-21]. Graphene, graphite, carbon nanotubes always show their superlubricity performance under nanoscale, which are fitting for Micro-Electro Mechanical System (MEMS), but may fail in industrial application due to the limit of bearing capacity. In addition, graphite can preserve superlubricity at microscale in open atmosphere, but disappear completely above a contact area of 4×108 nm^2 [19]. Although size limited effects on graphene have not been reported, how growth large-size of graphene is still a problem for industrial application [20].

Thus, to design and prepare superlubricious films could be a challenge. The exciting work of carbon-based films which is fitting industrial use has been reported by Erdemir et al. and

hydrogenated diamond-like films (H-DLC) films showed superlubricity properties in hydrogen or nitrogen atmosphere at macroscale [22-24]. However, the hydrogenated DLC films couldn't work in open atmosphere, and it is still a foot away for wide industrial use in open atmosphere, unless under particular conditions [24]. The exact breakthrough of superlubricity in open atmosphere condition was made by introducing graphene nanoscroll between interfaces in situ or out situ [25,26]. From the view of application, FL-C:H films have prominent advantages which can show superlubricity under open atmosphere conditions (with a lowest coefficient at 0.002) [25,26].

As early as 1995, fullerene-like nitride films (FL-CNx) were first prepared by Sjöström et al. [27]. A 30% nitrogen content is beneficial to the formation of onion-like structures, because the incorporation of nitrogen can promote the reduction of the potential barrier [28]. Afterwards, many methods (such as metal or non-metal doping, and adding nanostructures) have been applied to enhance the mechanical properties of H-DLC, and FL-C:H films have been obtained by adding fullerene-like nanostructures [29-36]. The first report of growth of FL-C:H films appeared in 2007 [37], and the first work about superlubricity of the film could be found in Ref. [12]. Due to the curvature structure of FL-C:H films, it extends the strength of graphite plane hexagon into three dimension space network, in turn, not only increasing the hardness and elasticity of carbon films, but also helping formation of graphene nanoscroll between interfaces. Thus, FL-C:H films can realize super low friction in air, meaning solid superlubricity owns engineering application value [26,28,37,38].

Growth Methods and Mechanisms

Here, two diagrams are depicted in Figure 1 to help understand the growth process of FL-C:H films. The first report of growth of FL-C:H films were using plasma enhanced chemical vapor deposition (PECVD) (Figure 1a). Seen from Figure 1a, a plate is grounded as an anode and the opposite plate connected with a power supply (which can be direct or pulsed current or

radiofrequency power supply). Besides, reactive magnetron sputtering (R-MS) can also be utilized to grow FL-C:H films [39,40]. Different from PECVD, there is a magnetron gun powered by a power supply, and substrate is powered by another one (Figure 1b). Compared comprehensively, R-MS can supply both third elements and extra power. Other methods to deposited FL-C:H films can be found in Ref. [41].

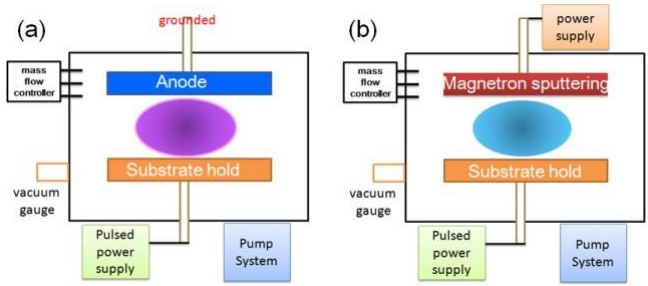

Figure 1: Growth methods for FL-C:H films: (a) plasma enhanced chemical vapour deposition and (b) reactive magnetron sputtering.

No matter what kind of methods, the most important factor is power supply to bias, that is, pulsed power supply can control the formation of fullerene-like structures, i.e., both the high bias and the pulse duty cycles (discussion later). Duty cycles determine the local relaxation of the distorted chemical bonds via turn-on/off time, which exactly control the growth process. Among them, the low pulse duty cycle could make the fullerene-like films have greater curvature nanostructures and the formation of a five-membered ring fraction, which is conducive to improving the mechanics propertise of FL-C:H films [42].

According to the typical sub-plantation model suggested by Robertson [43], three steps during ion interaction with the film are addressed: the cascade (10^{-14} s), the thermal spike (10^{-12} s), and the longer time relaxation (10^{-9} s). The longer relaxation time contributes the stress releasing and hydrogen removing which induces to rearrange of carbon matrix. In Zhang's work, a bias power supply with impulse frequency below 40 KHz was used and the annealing time was almost ~10^{-5} s, far than ~10^{-9} s. Therefore, the depositing film has a completely time restricting the formation of pentagonal rings which are related with the ion

bombardment at the pulse-on/off state (Figure 2) [42,44]. Besides, the R-MS methods own an extra power supply, the high impulse power is also necessary [39,40]. At low bias, only multilayer-graphene dispersed amorphous carbon (a-C) films was obtained, while at high bias, fullerene-like structures were obviously seen under high resolution transmission electron microscope (HRTEM) [38,45].

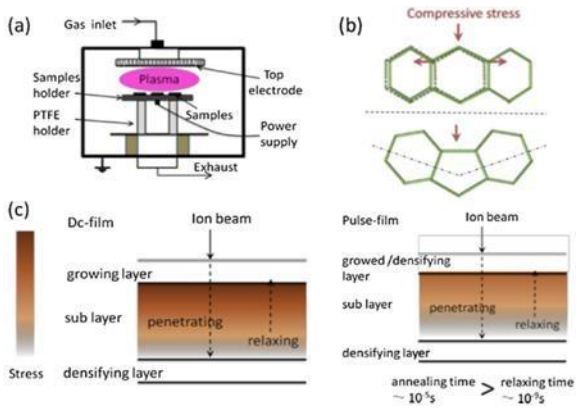

Figure 2: (a) The schematic diagram of the PECVD system. (b) Structural relaxation mechanism of the local distortions of the six-fold graphene rings by the creation of pentagonal rings in FL-C:H films. (c) Stress fields of depositing pulse- and dc- FL-C:H films. (Reproduced from Ref.42 with permission from the Royal Society of Chemistry).

The Factors Influencing to Nano-Structures

Generally, bias supply, atmosphere conditions and annealing dispose are factors that affect fullerene-like nanostructures. Carbon based films have versatile structures due to the bonding structures (sp, sp2 and sp3) were changing with the growth methods, which was in turn influenced by the power supply, atmospheres and with or without heating, etc. As mentioned above, both high bias as well as long pulse-off time are good for the unique structure formation of FL-C:H films. Thus, the high impulse power chemical vapour deposition (HiP-PECVD) is a prominent strategy for depositing FL-C:H films [21]. A typical HRTEM of FL-C:H films grown from HiP-PECVD is shown in Figure 3. One can see that curved graphene mixed in amorphous

matrix can hinder the slipping of grapheme by amorphous network. Due to the unique structure, the strength of graphite plane hexagon is extending into three dimension space network, meanwhile, FL-C:H films show the high hardness and high elastic recovery, thereby, endowing the films superlubricity at open air conditions. It is noteworthy that the fullerene-like structure could be adjusted via the hydrogen content, bias supply, deposition gas sources, and so on.

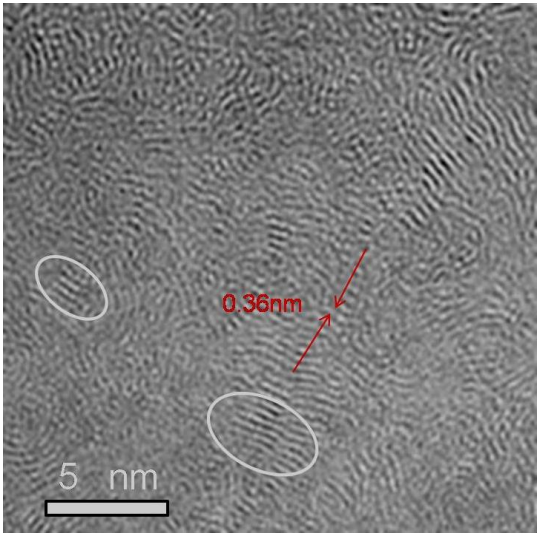

Figure 3: A typical HRTEM of FL-C:H films grown from HiP-PECVD.

For the purpose of formation in the fullerene-like nanostructures in FL-C:H films, bias supply, atmosphere conditions and annealing dispose are widely explored [46-49]. From bias side, high bias accompanying with long pulse-off time are crucial to the formation of curved graphene structures (proved both by HRTEM and Raman) for the FL-C:H films grown in PECVD system [21,42,44]. Similarly, R-MS owning high bias and pulse-off time can promote the FL-C:H films preparation, but the difference is that the target materials have some effects on nanostructure of the FL-C:H films [39,40]. When metal cathodes are employed, one can obtain multilayer-graphene dispersed a-C films at low bias and FL-C:H films at high bias [39,45]. Interestingly, when a carbon target is introduced, a-C films

replaced multilayer-graphene dispersed a-C films are obtained, but some bilayer- and trilayer- graphene are turning out after annealing, which means that, both metal targets might provide extra graphene as well as high-energy ions helping in situ rearranging are effectively [50]. Carefully, Researches showed that graphene based structure were growing on metal target surface (Figure 4), which were more active than pyrolytic carbon target that provided graphene flakes for the nanostructure carbon film growth [40,45].

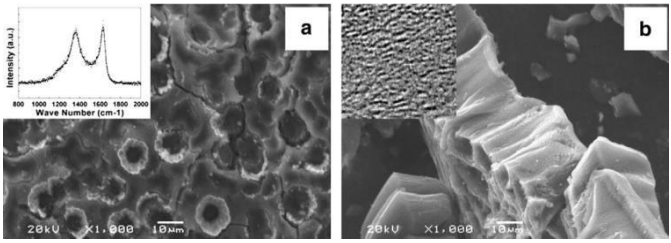

Figure 4: Plane-view FESEM image and the corresponding Raman spectrum (a), and cross-section FESEM image and the corresponding HRTEM image (b) of the films scratched off from Ni target. (Reproduced from Ref. 45 with permission from the Elesvier).

Another main influence on the nanostructures of FL-C:H films is growth atmospheres. Heterogeneous gases introducing in growth process, like hydrogen (H_2) and carbon tetrafluoride (CF_4), have different effects [47-49]. It is worth note that the growth of FL-C:H films show a conflict to Hellgren's work [51] that introduction of hydrogen will terminate potential bonding sites for CNx precursors and hinder the growth of fullerene-like structures. In the work of Wang et al., especially in PECVD process, hydrogen atoms are helpful in the manner of affecting the production of odd rings by two competing ways: (1) stress induced by H^+ leads to the introduction of odd ring into flat graphene plane; (2) H^+ ion preferentially etches the plane's sp^2 phase and destroys the bond basis. However, too much H_2 may deteriorate fullerene-like structures, so the effects of hydrogen need to be studied in detail [42,48]. Differently, CF_4 shows negative effects on the nonastructures that F-terminated large rings, branches and chains with sp^2 sites densify and start to

interact with each other and features like interlocking pore and amorphousness strongly prevail in the nanostructure [47,52].

Apart from power supply and atmospheres, extra heating in situ or out situ has great effects on the film nanostructures [50]. For carbon films, it is predicted that graphitization shows different response based on their original structures [53,54]. One can learn from Hellgren's work that heating helps booster fullerene-like structure growth [51]. And related research held the opinion that rapid annealing during the friction process can transform the structures of carbon films to generate new fullerene-like structures [55]. However, in some work, heating effects were scarcely concerned because their goals were aimed to industrial use. So, the degraded metal substrates may be aroused from heating which could be avoided. However, annealing effects after deposition were examined to help to understanding the changed trend of nano-structure. At 300 ℃, FL-C:H films showed the high harness as well as high elastic recovery, indicating that the most value of curved graphene exiting inside the carbon amorphous matrix (speculated from Raman results), which different from a-C films (no any change was observed after annealing at 300 ℃ [56,57]. Beyond 300 ℃, graphitization can occur because the degrade of crosslinking, which in turn induces the lowing of hardness [56,57]. Interestingly, recent studies have found that FL-C:H films were annealed at 200-500℃ under nitrogen protection, and the films had achieved superlubricity at different annealing temperatures. It was also found that thermal induction made the nanostructures more ordered [58]. In addition to the previously mentioned HRTEM, Raman spectroscopy is another effective method to obtain the topological structure of carbon films. FL-C:H films exhibit typical character of DLC films in the region of 1000~2000 cm^{-1}, shown in Figure 5, but with some versatile bands at about 400 and 700 cm^{-1} and a distinct shoulder at around 1230 cm^{-1}.

The two low intermediate wave number bands near 400 cm^{-1} and 700 cm^{-1} are very similar to that of fullerene like carbon nitride (FL-CNx) films that can be attributed to relaxation of Raman selection rule because of the curvature in graphene planes [59]. The same bands can also be observed in the Raman spectra for

carbon onions and C_{60} that have been attributed to the transverse optic and transverse acoustic vibrations [60]. Thus, combined with HRTEM images, an acceptable fitting lines could be carried out via four Gaussian peaks at about 1230, 1350, 1470, and 1560 cm^{-1}, respectively [12,37,39,40]. Thus, all peaks at around 400, 700, 1230 and 1480 cm^{-1} can be considered that all active from curled graphene flakes in FL-C:H films.

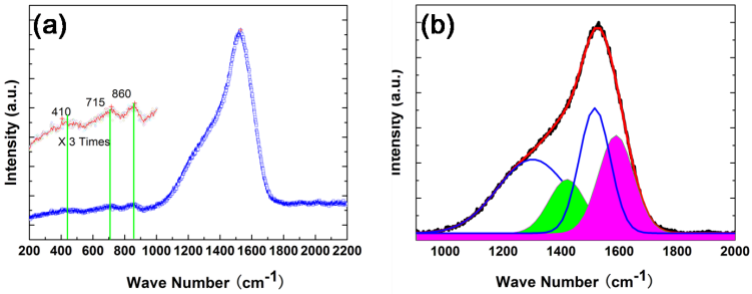

Figure 5: Raman spectra of hydrogenated carbon film deposited by dc- pulse plasma CVD: (a) Raman spectrum and magnified wave number region from 0 to 1000 cm^{-1} and (b) four bandsfitting of the Raman spectrum of (a) in region from 1000 to 2000 cm^{-1}.

Friction Performance and Superlubricity

FL-C:H films have excellent mechanical properties with high hardness and high elastic recovery due to the existence of fullerene-like structures [61-64]. At the same time, fullerene-like structures can improve the performance of a-C: H in wet and inert environments. The onion-like structures largely determine the appearance of superlubricity and greatly improves the wear resistance [37,65,66]. Superlubricity was firstly reported that superlow friction (coefficient at 0.009) could reach under load of 20 N. The loads effects on the friction were carefully studied in Ref. [67]. Liu et. al. studied the relationship between sliding speed and superlubricity on H-DLC films. In air, sliding speed has a negative correlation with friction and wear. As the sliding speed increases, the friction and wear value firstly decrease to a minimum and then increase, due to the synergistic effect of the transfer films and the passivation effect [68]. In vacuum, low sliding speed is beneficial for maintaining superlubricity [69].

However, for FL-C:H films prepared by magnetron sputtering have a lifetime of 36000 times in a vacuum environment due to the presence of the fullerene-like structures and the formation of onion carbon during friction, it can be known from the work of Song et al. [64]. The life is affected by the poor adhesion between FL-C:H films and steel, which can be solved by incorporating iron particles [70]. The friction coefficient decrease with load was reported everywhere though no superlubricity was observed [71]. The conversion from low friction to super-low friction can also be achieved by increasing the normal load [72]. In comparison, H-DLC films have a threshold load in a humid environment, and the friction force does not significantly change below the threshold value. When the load is above the threshold value, the friction force significantly decreases with the load increased. In vacuum, low load could keep the interface transfer layer for a long time, so low load is beneficial to achieve low friction [73]. Deeply study showed that some special nanostructure was forming during friction. This is a huge difference from a-C(:H) film due to the particular of nanostructures [15,21,26,38,74].

To understanding how the effects of fullerene-like structure on the tribological properties. X-ray diffraction (XRD) analysis, HRTEM and Raman Spectroscope have been performed at the original surface and wear debris and tracks of FL-C:H films. XRD pattern shows three peaks at about 2θ=69.1°, 33°, and 22.4°. The two peaks at 2θ=69.1° and 33° are from the silicon substrate [004] and [002], respectively (Figure 6). other studies considered a weak peak at 2θ=22.4° which can be ascribed to fullerene-like or onion-like nanoparticles [74]. And after friction tests, the peak at 2θ=22.4° become prominent, accompanying with a new band at 2θ=15° which arise from fullerene-like or onion-like nanoparticles. It was further confirmed by HRTEM that onions as well as fullerene-like carbon were observed in FL-C:H films. A well- structured carbon onions can play as a "molecular bearing" during the friction process, and achieve macroscopic superlubricity in a humid environment, owing to the incommensurate contact achieved by carbon onions [75]. In addition, the advantage of fullerene-like to superlubricity can be deduced from the friction properties of fluorine atom (F)

incorporation which destroys the fullerene-like structures via F-terminating. Therefore, the friction coefficient increases with the amount of F content in carbon films. Besides, the effects of F incorporation, the humidity variation on the tribology properties of FL-C:H films were widely studied [46,47,49,52,61,76-78]. Unfortunately, humidity has a great influence on friction coefficients, that is, with increasing the humidity, the friction coefficient increases quickly to 0.07 at 50% for humidity (using GCr15 ball as couple). HRTEM results show that the onion-like nanoparticles in the debris are restrained: from spherical shell structure below 30% humidity to short curved graphene dispersed in amorphous matrix [21,26]. However, humidity effects on superlubricity vary with couple materials. As shown in Figure 7, in the dry open air, Al_2O_3, Steel (GCr15) and Si_4N_3 balls are used as couples, all of them can reach superlubricity under load scope of 2 to 20 N, but the superlubricity property only can keep under humidity of 30%. HRTEM images proved that higher humidity suppressed the formation of onions or fullerene-like structures beyond the humidity of 30%, accompanying with disappearance of superlubricity. It can also conclude that superlubricity is strongly related with couple materials. Recently, Zhang's group showed that couple ball with a-C(:H) film surface could widen the superlubricity scope [79].

In order to further reveal superlubricity phenomenon FL-C:H films, the interface structure evolution was studied on the debris. Surprisingly, multilayer graphene nanoparticles (GNPs) were observed in wear debris. It can be proposed that the formation mechanism of GNPs is the self-organization of graphene sheets, which can be divided into two steps, nucleation and growth, respectively. The nucleation of GNPs core is similar to the reaction pathway from graphene-to-fullerene, since the molecular cage of fullerene is more stable than graphene [80,81]. However, the driving force of the process is not high temperature but friction shear force. A possible nucleation and growth mode is given in Figure 8. The nucleation process can be divided into four stages: (1) At initial stage, the dual surface and the film have strong coupling, resulting in strong wear and a large number of wear debris. The graphene layers (Figure 8a) peeled off from the bulk body and direct contacted with the dual surface

(Figure 8f). (2) Subsequently, these graphene sheets (Figure 8b) is folded and coiled under the shear stress (Figure 8g). (3) With the development of friction process, these short range graphene fragments are coiled to form a cage-like structure under the action of periodic shearing force (Figure 8h). (4) After more friction cycles, the carbon cage structure becomes more regular (Figure 8i), position 2 and 3 (Figure 8c) marks a monolayer and a double layer, respectively. The single wall carbon cage diameter is about 0.7 nm, which has a similar radius to C60 (0.71nm).

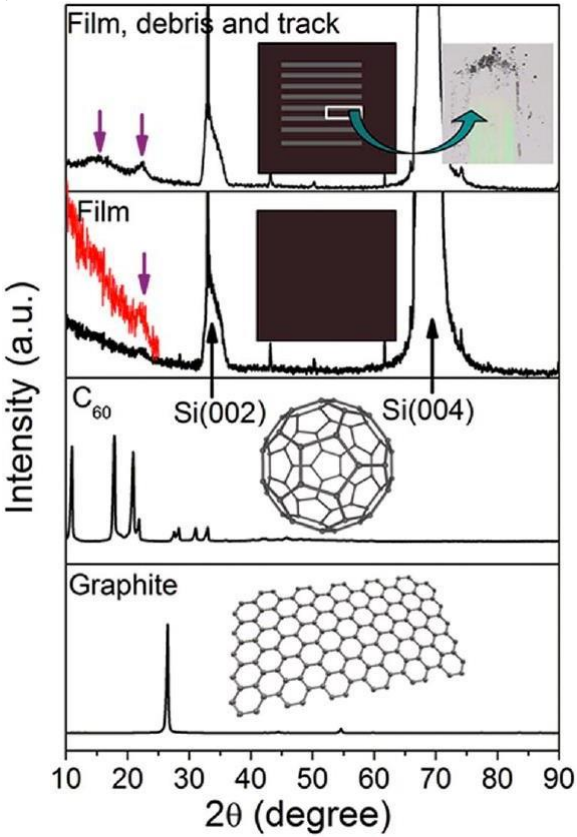

Figure 6: Experiment XRD patterns from the film and wear debris showing that the debris has a structure analogous to that of C_{60}, far from that of nc-graphite. (Reproduced from Ref. 75 with permission from the Royal Society of Chemistry).

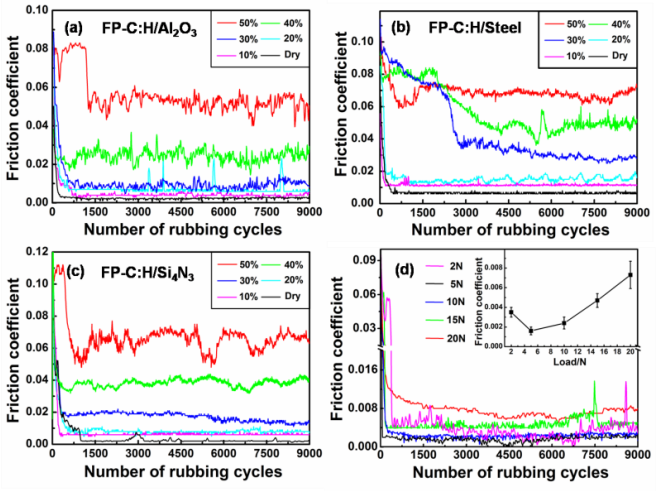

Figure 7: (a), (b) and (c) The friction coefficient curves as a function of rubbing cycles at different humidity against Al_2O_3, Si_4N_3, and steel ball,respectively. (d) Friction coefficient curves of the FP-C:H films in a dry air atmosphere under a load from 2 N to 20 N, the inset shows the frictioncoefficient as a function of load. (Reproduced from Ref. 21 with permission from the Royal Society of Chemistry).

The growth mechanism can be surmised from the HRTEM images of wear debris, the defected graphene layers (soft) are easy to package fullerene core (hard), which is similar to the mechanism reported by Anirudha et al. [25]. The growth model of GNPs was similar to the snowball effect. When the friction process tends to reach a balance, the thermodynamic non-equilibrium state of fingerprint like-carbon (FP-C:H) films tend to reach an equilibrium state. A large class of GNPs can be formed after 3000 friction cycles (Figure 8d). Few GNPs layers (position 4) can be found on the edge of a big particle, which can be seen as the evidence of this form of nucleation and growth pattern. Raman spectra of original films and wear debris of 600, 1200 and 6000 friction cycles also confirmed this growth model (Figure 8e), since the I_{2D}/I_D+G+I_{2D} increased. Figure 8j, k, l and m are a possible growing model. Due to the spontaneous reduction of surface energy, the graphene sheets tend to wrap around the carbon cage core to reduce the surface area (Figure 8j and k). Under the effect of shear stress, the bonding

recombination occurs at the interface, and finally leads to the formation of multilayer GNPs (Figure 8l and m).

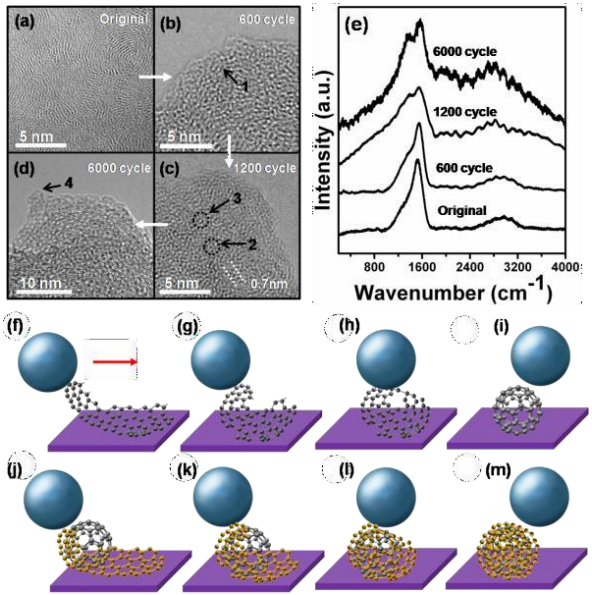

Figure 8: (a) HRTEM images of original FP-C:H films . (b), (c) and (d) wear debris of 600, 1200 and 6000 friction cycles, at 10N, 10Hz. (e) Raman spectra of original films and wear debris of 600, 1200 and 6000 friction cycles, respectively. (f), (g), (h), (i), (j), (k), (l) and (m) Schematic diagram of nucleation and growth model for GNPs. (Reproduced from Ref. 21 with permission from the Royal Society of Chemistry).

Potential Industrial Applications

Recently, Holmeberg et al. have published papers to state the current austere condition about friction induced energy loss in passenger cars and engineering plants [80,81]. They come into a conclusion that friction accounts one third of the engine's fuel energy consumption, which is a main problem conflicting to energy save and emission reduction. Thanks to the great tribology properties of DLC or carbon-based films, many attempts and efforts has donated to using such films in engine systems to save energy and reduce emission, and surely some progresses are made [82-84].

Figure 9: Some photos from FL-C:H films coated samples.

As a prominent anti-wear and anti-friction materials, FL-C:H films has more attractive in dealing with energy conservation and emission reduction of engine. For this great purpose, our group have in hand with FAW Group Corp., the biggest auto manufacturer in China, to push superlubricous FL-C:H films in engine use to energy-saving reduction strategic Strategy. Engine parts, like valve tappet, plunger, piston ring, pin valve and bearings were coated with FL-C:H films in our lab (Figure 9). Even some of them realize mass production. Figure 10 shows a bench test example that valve tappet with or without FL-C:H films run for more than 100 times on a home-made electrically driven valve train test rig in China Faw Group Corporation R&D Center. The results show that friction factor of the FL-C:H films coated valve train was reduced by 67% and the ability of wear resistance was enhanced [85,86]. Friction loss of engine valve train was decreased by 6%. Thanks to the excellent FL-C: H film, engine component makes engines more efficient and suitable for the low carbon technical route.

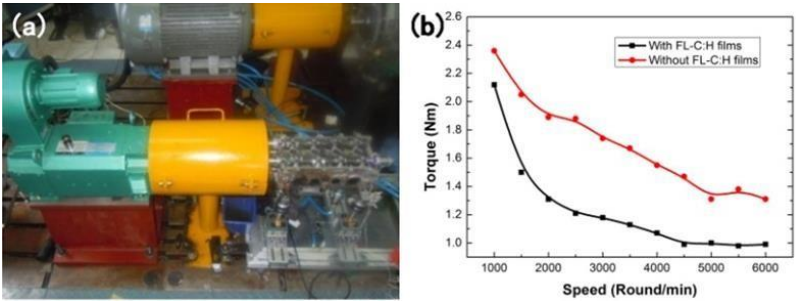

Figure 10: Bench test for valve tappet with or without FL-C:H films.

Conclusion and Prospection

In summary, deposition strategies, growth mechanism, the factors to superlubricity and its inner-mechanism for FL-C:H films are all discussed in this chapter. One of the great advantages is that FL-C:H films can be grown via PECVD, ECR-PECVD and R-MS methods, and all of them are suitable for mass production, providing basic conditions for the practical application of that films. The superlubricity of FL-C:H films are arisen from their excellent mechanical properties and unique bulk structure, which can provide graphene flakes to form carbon onions or scrolls to afford micro-bearing, achieve incommensurate contact and reduce shear force in interfaces. FL-C:H films exhibit low or super-low friction properties in a variety of environments including humidity, atmosphere, and vacuum etc., which determines the its application. Combined all these merits, FL-C:H films are considered as a good candidate for widely industrial use. Furtherly, collaborating with FAW Group Corp., kinds of engine parts were coated with FL-C:H films which were tested on bench or even using on real engine, and it proves that benefit from superlbubricious FL-C:H films, engine component makes engines more efficient and suitable for the low carbon technical route. Superlubricity under open atmosphere can be realized by introduce of fullerene-like structures into amorphous carbon matrix, which open the way to save energy and reduce emission for many mechanical units without special conditions by superlubricity technology. When (before/during friction) and where (application) should fullerene-

like structures be in what way (composite or interface introduction) are worth to studying, such as: (1) introducing fullerene-like structures in some application-deficient materials to improve friction performance. (2) Generating or adding fullerene-like structures in the friction interface can regulate friction or availability period. In addition to saving energy by reducing friction, the expanded use of fullerene-like films or containing fullerene-like structures materials may be considered for some high-end equipment.

References

1. O Hod, E Meyer, Q Zheng, M Urbakh. Structural super lubricity and ultra-low friction across the length scales. Nature. 2018; 563: 485-492.
2. A Erdemir, O Eryilmaz. Achieving superlubricity in DLC films by controlling bulk, surface, and tribochemistry. Friction. 2014; 2: 140–155.
3. Spalvins T. Lubrication with sputtered MoS_2 films: Principles, operation, and limitations [J]. 1992, 1(3):347-351.
4. Y Niiyama, T Takeno, K Kurihara, K Adachi. Effect of sliding history on super-Low Friction of diamond-like carbon coating in water lubrication, Tribol. Lett. 2017; 65: 63.
5. X Feng, S Kwon, JY Park, M Salmeron. Superlubric sliding of graphene nanoflakes on graphene, ACS Nono. 2013; 7: 1718-1724.
6. S Miyake. Tribological properties of hard carbon films-extremely low friction mechanism of amorphous hydrogenated carbon films and amorphous hydrogenated SiC films in vacuum, Surf. Coat. Technol. 1992; 45-55: 563-569.
7. J Li, J Luo. Advancements in superlubricity, Sci. China, Tech. Sci. 2013; 56: 2877-2887.
8. M Hirano, K Shinjo. Atomistic locking and friction. Phys. Rev. B. 1990; 41: 11837.
9. M Hirano, K Shinjo, R Kaneke, Y Murata. Anisotropy of friction forces in muscovite mica. Phys. Rev. Lett. 1991; 67: 2642.

10. M Hirano, K Shinjo. Superlubricity and frictional anisotropy. Wear. 1993; 168: 121-125.
11. TB Ma, YZ Hu, L Xu, LF Wang, H Wang. Shear-induced lamellar ordering and interfacial sliding in amorphous carbon films: A superlow friction regime. Chem. Phys. Lett. 2011; 514: 325-329.
12. C Wang, S Yang, Z Wang, J Zhang. Super-low friction and super-elastic hydrogenated carbon films originated from a unique fullerene-like nanostructure. Nanotechnology. 2008; 19: 225709.
13. J Li, C Zhang, L Ma, Y Liu, J Luo. Superlubricity Achieved with Mixtures of Acids and Glycerol. Langmuir. 2012; 29: 271-275.
14. X Liu, J Yang, J Hao, J Zheng, Q Gong, et al. Near frictionless and extremely Elastic hydrogenated amorphous carbon film with self-assembled dual nanostructure. Adv. Mater. 2012; 24: 4614-4617.
15. Z Gao, W Zhao, A Liang, J Zhang. A general engineering applicable superlubricity: hydrogenated amorphous carbon film containing nano diamond particles. Adv. Mater. Interfaces. 2017; 4: 1601224.
16. W Ma, Z Gong, K Gao, L Qiang, J Zhang, et al. Superlubricity achieved by carbon quantum dots in ionic liquid. Mater. Lett. 2017; 195: 220-223.
17. SW Liu, HP Wang, Q Xu, TB Ma, G Yu, et al. Robust microscale superlubricity under high contact pressure enabled by graphene-coated microsphere, Nat. Commun. 2017; 8: 14029.
18. R Zhang, Z Ning, y Zhang, Q Zheng, Q Chen, et al. Superlubricity in centimetres-long double-walled carbon nanotubes under ambient conditions. Nature Nanotechnology. 2013; 8: 912-916.
19. CC Vu, S Zhang, M Urbakh, Q Li, QC He, et al. Observation of normal-force-independent superlubricity in mesoscopic graphite contacts, Phys. Rev. B. 2016; 94: 081405R.
20. D Dietzel, J Brndiar, I tich, A Schirmeise. Limitations of Structural Superlubricity:Chemical Bonds versus Contact Size. ACS Nano. 2017; 11: 7642-7647.

21. Z Gong, J Shi, W Ma, B Zhang, J Zhang. Engineering- scale superlubricity of the fingerprint-like carbon films based on high power pulsed plasma enhanced chemical vapor deposition. RSC Adv. 2016; 6: 115092.
22. A Erdemir, OL Eryilmaz, G Fenske. Synthesis of diamondlike carbon films with superlow friction and wear properties. J. Vac. Sci. Technol. A. 2000; 18: 1987.
23. A Erdemir, OL Eryilmaz, IB Nilufer, G Fenske. Synthesis of superlow-friction carbon films from highly hydrogenated methane plasmas. Surf. Coat. Technol. 2000; 133-134: 448-454.
24. A Erdemir. The role of hydrogen in tribological properties of diamond-like carbon films. Surf. Coat. Technol. 2001; 146-147: 292-297.
25. D Berman, SA Deshmukh, SKR Sankaranarayanan, A Erdemir, AV Sumant. Macroscale superlubricity enabled by graphene nanoscroll formation. Science. 2015; 348: 1118-1122.
26. Z Gong, J Shi, B Zhang, J Zhang. Graphene nano scrolls responding to superlow friction of amorphous carbon. Carbon. 2017; 116: 310-317.
27. Sjöström H, Stafström S, Boman M, Sundgren J. Superhard and Elastic Carbon Nitride Thin Films Having Fullerene like Microstructure. Phys. Rev. Lett. 1995; 75: 1336-1339.
28. L Hultman, J Neidhardt, N Hellgren, H Sjöström, J Sundgren. Fullerene-like CarbonNitride: A Resilient Coating Material.
29. K Zhou, P Ke, X Li, Y Zou, A Wang. Microstructure and electrochemicalproperties of nitrogen-doped DLC films deposited by PECVD technique. Carbon. 2015; 329: 281–286.
30. A Erdemir, O Eryilmaz. Achieving superlubricity in DLC films by controlling bulk,surface, and tribochemistry. Friction. 2014; 2: 140–155.
31. K Oguri, T Arai. Tribological properties and characterization of diamond-likecarbon coatings with silicon prepared by plasma-assisted chemical vapour deposition, Surf. Coat. Technol. 1991; l47: 710–721.
32. G Ma, S Gong, G Lin, L Zhang, G Sun. A study of structure and properties of Tidoped DLC film by reactive magnetron

sputtering with ion implantation. Appl. Surf. Sci. 2012; 258: 3045–3050.
33. W Dai, P Ke, A Wang. Microstructure and property evolution of Cr-DLC films withdifferent Cr content deposited by a hybrid beam technique. Vacuum. 2011; 85: 792–797.
34. A Banerji, S Bhowmick, AT Alpas. High temperature tribological behavior of Wcontaining diamond-like carbon (DLC) coating against titanium alloys. Surf. Coat. Technol. 2014; 241: 93–104.
35. Y Wang, K Gao, B Zhang, Q Wang, J Zhang. Structure effects of sp2-richcarbon films under super-low friction contact. Carbon. 2018; 137: 49–56.
36. C Wang, B Li, X Ling, J Zhang. Superlubricity of hydrogenated carbonfilms in a nitrogen gas environment: adsorption and electronic interactions at the sliding interface. RSC Adv. 2017; 7: 3025–3034.
37. Q Wang, C Wang, Z Wang, J Zhang, D He. Fullerene nanostructure-induced excellent mechanical properties in hydrogenated amorphous carbon. Appl. Phys. Lett. 2007; 91: 141902.
38. J Shi, Y Wang, Z Gong, B Zhang, C Wang, et al. Nanocrystalline graphite formed at fullerene-like carbon film friction interface. Adv. Mater. Interfaces. 2017; 4: 1601113.
39. P Wang, X Wang, B Zhang, W Liu. Structural, mechanical and tribological behavior of fullerene-like carbon film. Thin Solid Films. 2010; 518: 5938-5943.
40. P Wang, X Wang, B Zhang, W Liu. Formation of hydrogenated amorphous carbon films containing fullerene-like structures. J. Non-Cryst. Sol. 2009; 355: 1742-1746.
41. Direct spectroscopic evidence of self-formed C_{60} inclusion in a fullerene-like hyrogenated carbon films. Appl. Phys. Lett. 2008; 92.
42. Y Wang, K Gao, J Shi, J Zhang. Bond topography and nanostructure of hydrogenated fullerene-like carbon films: A comparative study, Chem. Phys. Lett. 2016; 660: 160-163.
43. J Robertson. Mechanism of sp3 bond formation in the growth of diamond-like carbon, Diam. Relat. Mater. 2004; 14: 942-948.

44. G Liu, Y Zhou, B Zhang, K Gao, L Qiang, et al. Monitoring the nanostructure of a hydrogenated fullerene- like film by pulse bias duty cycle. RSC Adv. 2016; 6: 59039-59044.
45. J Zhang, B Zhang, Q Xue, Z Wang. Ultra-elastic recovery and low friction of amorphous carbon films produced by dispersion of multilayer grapheme. Diam. Relat. Mater. 2012; 23: 5-9.
46. J Wang, Z Cao, F Pan, F Wang, A Liang, et al. Tuning of the microstructure, mechanical and tribological properties of a-C:H films by bias voltage of high frequency unipolar pulse. Appl. Surf. Sci. 2015; 356: 695-700.
47. L Zhang, J Wang, J Zhang, B Zhang. Increasing fluorine concentration to control the microstructure from fullerene-like to amorphous in carbon films. RSC Adv. 2016; 6: 21719-21724.
48. Y Wang, J Guo, K Gao, B Zhang, A Liang, et al. Understanding the ultra-low friction behavior of hydrogenated fullerene-like carbon films grown with different flow rates of hydrogen gas. Carbon. 2014; 77: 518-524.
49. L Qiang, B Zhang, K Gao, Z Gong, J Zhang. Hydrophobic, mechanical, and tribological properties of fluorine incorporated hydrogenated fullerene-like carbon films. Friction. 2013; 1: 350-358.
50. B Zhang, Y Zhou, J Zhang, Z Wang. The effect of thermal annealing on the microtructure and mechanical properties of mechanical properties of magnetron sputtered hydrogenated amorphous carbon fims. Surf. Interface Anal. 2012; 44: 162-165.
51. N Hellgren, MP Johansson, B Hjörvarsson, M Östblom, B Liedberg, et al. Growth, structure, and mechanical properties of CNxHy films deposited by dc magnetron sputtering in $N_2/Ar/H_2$ discharges. J. Vac. Sci. Technol. A. 2000; 18: 2349.
52. L Wei, B Zhang, Y Zhou, L Qiang, J Zhang. Ultra-low friction of fluorine- doped hydrogenated carbon film with curved graphitic structure. Surf. Interface Anal. 2013; 45: 1233-1237.
53. K Lee, H Ki. Rapid fabrication of transparent conductive films with controllable sheet resistance on glass substrates

by laser annealing of diamond-like carbon films. Acta Mater. 2016; 111: 315-320.
54. T Laurila. Diamond-like carbon thin film bioelectrodes: Effect of thermal post-treatments and use of Ti adhesion layer. Mater. Sci. Eng. C. 2014; 34: 446-454.
55. J Guo, Y Wang, H Liang, A Liang, J Zhang. Mechanical properties and tribological behavior of fullerene-like hydrogenated carbon films prepared by changing the flow rates of argon gas. Appl. Surf. Sci. 2016; 364: 288-293.
56. Z Wang, C Wang, Q Wang, J Zhang. Annealing effect on the microstructure modification and tribological properties of amorphous carbon nitride films. J. Appl. Phys. 2008; 104: 073306.
57. Q Wang, D He, C Wang, Z Wang, J Zhang. The evolution of the structure and mechanical properties of fullerene like hydrogenated amorphous carbon films upon annealing. J. Appl. Phys. 2008; 104: 043511.
58. Z Wang, Z Gong, B Zhang, Y Wang, K Gao, et al. Heating induced nanostructure and superlubricity evolution of fullerene-like hydrogenated carbon films. Solid. Sta.Sci. 2019; 90: 29-33.
59. DG Liu, JP Tu, CD Gu, CF Hong, R Chen, WS Yang. Synthesis, structure and mechanical properties of fullerene-like carbon nitride films deposited by DCmagnetron sputtering. Surf. Coat. Technol. 2010; 205: 2474-2482.
60. D Roy, M Chhowalla, H Wang, N Sano, I Alexandrou, et al. Characterisation of carbon nano-onions using Raman spectroscopy. Chem. Phys. Lett. 2003; 373: 52-56.
61. K Wu, L Qiang, Z Gong, G Zhao, K Gao, et al. The tribological performance of fullerene-like hydrogrnate carbon films under ionic liquid lubrication. Surf. Interface Anal. 2015; 47: 903-910.
62. Q Wang, C Wang, Z Wang, J Zhang, D He. Fullerene nanostructure-induced excellent mechanical properties in hydrogenated amorphous carbon. Appl. Phys. 2007; 91: 141902.
63. Y Wang, K Gao, Q Wang, J Zhang. The correlation between nano-hardness and elasticity and fullerene-like clusters in hydrogenated amorphous carbon films. Chem. Phys. Lett. 2018; 692: 258-263.

64. H Song, J Chen, Z Liu, L Ji, H Li, et al. Fullerene-like nanostructure induced excellent friction behavior in high vacuum environment for hydrogenated carbon film. Vacuum. 2017; 143: 36-39.
65. Z Gong, C Bai, L Qiang, K Gao, J Zhang, et al. Diam. Relat. Mater. 2018; 87: 172-176.
66. L Ji, H Li, F Zhao, W Quan, J Chen, et al. Fullerene-like hydrogenated carbon films with super-low friction and wear, and low sensitivity to environment. J. Phys. D Appl. Phys 2010; 43: 015404.
67. Z Wang, C Wang, B Zhang, J Zhang. Ultralow friction behaviours of hydrogenated fullerene-like carbon films: effect of normal load and surface tribochemistry. Tribol. Lett. 2011; 41: 607-615.
68. Y Liu, B Zhang, L Chen, Z Cao, P Shi, et al. Coating, Perspectives of the Friction Mechanism of Hydrogenated Diamond-Like Carbon Film in Air by Varying Sliding Velocity. 2018; 8: 331.
69. Y Liu, B Yu, Z Cao, P Shi, N Zhou, et al. Probing superlubricity stability of hydrogenated diamond-like carbon film by varying sliding velocity. Appl. Surf. Sci. 2018; 4332: 30051-30055.
70. Y Wang, Z Yue, Y Wang, J Zhang, K Gao. Synthesis of fullerene-like hydrogenated carbon films containing iron nanoparticles. Mater. Lett. 2018; 219: 51-54.
71. L Qiang, K Gao, L Zhang, J Wang, B Zhang, et al. Further improving the mechanical and tribological properties of low content Ti-doped DLC film by W incorporating, Appl. Surf. Sci. 2015; 353: 522-529.
72. Z Yue, Y Wang, J Zhang. Microstructure changes of self-mated fullerene-like hydrogenated carbon films from low friction to super-low friction with the increasing normal load. Diam. Relat. Mater. 2018; 88: 276-281.
73. Y Liu, L Chen, B Zhang, Z Cao, P Shi, et al. Key Role of Transfer Layer in Load Dependence of Friction on Hydrogenated Diamond-Like Carbon Films in Humid Air and Vacuum. Mater. 2019; 12: 1550.
74. Y Wang, J Guo, J Zhang, Y Qin. Ultralow friction regime from the in situ production of a richer fullerene-like

nanostructured carbon in sliding contact. RSC Adv. 2015; 25: 106476-106484.
75. Z Gong, C Bai, L Qiang, K Gao, J Zhang, et al. Onion- like carbon films endow macro-scale superlubricity. Diam. Relat. Mater. 2018; 87: 172-176.
76. X Wang, P Wang, B Zhang, S Yang, J Zhang. The tribological properties of fullerene-like hydrogenated carbon (FL-C: H) film under different humidity conditions. Tribology Transactions. 2009; 52: 354-359.
77. Y Wang, B Zhang, Z Gong, K Gao, Y Ou, et al. The effect of a static magnetic field on the hydrogen bonding in water using frictional experiments. J. Mol. Struct. 2013; 1052: 102-104.
78. J Shi, Z Gong, C Wang, B Zhang, J Zhang. Tribological properties of hydrogenated amorphous carbon films in different atmospheres. Diam. Relat. Mater. 2017; 77: 84- 91.
79. Y Wang, Y Wang, X Zhang, J Shi, K Gao, et al. Hydrogenated amorphous carbon films on steel balls and Si substrates: nanostructural evolutions and their trigging tribological behaviors. Appl. Surf. Interfaces. 2017; 420: 586-593.
80. A Chuvilin, U Kaiser, E Bichoutskaia, NA Besley, AN Khlobystov. Direct transformation of graphene to fullerene. Nature Chemistry. 2010; 2: 450-453.
81. JY Huang, F Ding, K Jiao, BI Yakobson. Real time microscopy, kinetics, and mechanism og giant fullerene evaporation. Phys. Rev. Lett. 2007; 99: 175503.
82. K Holmberg, P Andersson, A Erdemir. Global energy consumption due to friction in passenger cars. Tribol. Int. 2012; 47: 221-234.
83. K Holmberg, P Kivikytö-Reponen, P Härkisaari, K Valtonenb, A Erdemirc. Global energy consumption due to friction and wear in the mining industry. Tribol. Int. 2017; 115: 116-139.
84. SV Johnston, SV Hainsworth. Effect of DLC coatings on wear in automotive applications. Surf. Eng. 2005; 21: 67- 71.
85. Y An, K Zhang, D Wang, J Zhang, B Zhang. Advanced Solid Lubricant Technology Improve Engine Performance. Proceedings of the FISITA 2012 World Automotive Congress. 2012; 839-849.

86. B Wu, J Li, J Zhang, B Zhang. Fabrication and properties of tappet with diamond-like carbon films. J. Jilin University (Engineering and Technology Edition). 2013; 43: 51-55.