



The effect of hydrogen on the tribological behavior of diamond like carbon (DLC) coatings sliding against Al₂O₃ in water environment

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ABSTRACT

The tribological behavior of hydrogenated and hydrogen free diamond like carbon (DLC) coatings sliding against Al₂O₃ in air and pure water was investigated by ball-on-disc reciprocation wear test, and the effect of hydrogen was discussed. The results showed that in air environment, the Al₂O₃ slide against DLC under solid lubrication condition, and the wear of DLC coatings was mainly affected by coating mechanical properties. The hydrogen lowered the coating hardness and brought more DLC wear in air environment. In water environment, the solid lubrication effect is weak, the hydrogen began to play an important role in DLC wear. The hydrogenated DLC coating with saturated -CH bonds showed better wear resistance even though its hardness is lower. The hydrogenated DLC coating with unsaturated -CH bonds was easy to graphitize and generate massive wear no matter in water or in air environment.

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1. Introduction

Artificial joint has been used to cure joint traumas and joint diseases since last century. In 2011, FDA approved the first ceramic-on-metal (COM) type artificial joint system for patients with orthopedic diseases. In comparison with metal-on-polymer (MOP) type and metal-on-metal (MOM) type artificial joints, the COM one exhibits a reduced friction and wear because of smoother surfaces, improved lubrication and lower corrosive wear [1]. However, recent study declares COM type artificial joint is a highly sensitive wear couple, the high variation of wear between individuals may indicate potential problems in-vivo [2]. Additionally, a recent clinical study for COM artificial joint demonstrated that metal ion levels were significantly elevated at midterm follow-up [3]. The wear debris and metal ions may result in adverse biological reactions [4]. In order to reduce the wear and ion release, diamond like carbon (DLC) coating is promised to protect the metal component in COM artificial joint due to its wear resistance, chemical inertness and biocompatibility.

The tribological behavior of DLC coating is sensitive to the environment and coating identity. In vacuum or inert atmosphere, hydrogen free DLC coating shows relatively high friction and heavy wear because of strong covalent bond interactions between its free σ -bonds and atoms in counterpart ball [5]. Oppositely, hydrogenated DLC coating

shows low friction and slight wear due to the elimination of free σ -bonds by hydrogen. In humid air, the friction coefficient of the hydrogenated DLC coating increases with increasing humidity due to the interruption of lubricating layer and friction induced coating oxidation [6]. However, hydrogen free DLC coating can keep a low friction coefficient in humid environment because the water molecular will terminate the free σ -bonds on the coating surface [7].

In water environment, water molecules will react with hydrogenated and hydrogen free DLC coating forming oxygen containing hydrophilic group at the sliding surface [8]. These hydrophilic groups will produce a surface layer rich in water, providing lubrication for the counter surfaces. As a result, both the hydrogenated and hydrogen free DLC coatings show lower friction coefficient in water than that in air [9, 10]. In water environment, hydrogenated DLC coating generally shows a higher specific wear rate than in air environment [9,11]. However, opposite conclusion can be found in Ref. [12], which shows a lower wear rate of hydrogenated DLC coating in water environment than in air environment. Hydrogen free DLC coating is reported to perform well in water environment, but its high hardness may cause wear of the counterface material [13]. For hydrogenated and hydrogen free DLC coatings, there is still no final conclusion about which one is more suitable for the application in water environment.

In physiological environment, water, inorganic salt and organic biological molecule will influence the wear of DLC coating and the wear mechanism is very complicated. In the initial stage, we only focused on the tribological behavior of DLC coatings in pure water, and the effect

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of hydrogen was discussed. The wear behavior of DLC in air environment was also investigated as control.

2. Experimental

2.1. Coating preparation and characterization

Biomedical CoCrMo alloy wafers with 14 mm diameter and 1.5 mm thickness were used as the substrates. Before the DLC deposition, the substrate was grinded and polished to a roughness of 2 – 10 nm. Then hydrogenated and hydrogen free DLC coatings were prepared on the CoCrMo substrates by plasma immersion ion deposition (PIID, labeled as HD1) [14], electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD, labeled as HD2) [15] or filtered cathode vacuum arc (FCVA, labeled as D3) [16], respectively. The coating thickness and roughness were measured by a step profiler (XP2, AMBIOS, USA) and atomic force microscope (CSPM 5000, BenYuan, China). The hydrogen content of HD1 and HD2 was measured by elastic recoil detection analysis (ERDA, NEC/9SDH-2, China). The indentation hardness and modulus of the DLC coating were evaluated by indentation test using a dynamic ultra micro hardness tester (DUH-211S, Japan). Load-unload curves were measured to calculate the indentation hardness and modulus, as described in Ref. [17]. The properties of DLC films mentioned above are shown in Table 1. The structure of the DLC coatings was characterized by Raman spectroscopy ($\lambda = 514$ nm, Renishaw Invia, UK). The C-H bonds in the DLC coatings were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, US).

2.2. Tribological properties of the DLC coating

The tribological properties of the DLC coatings were tested by a ball-on-disc tribometer (CSEM, Switzerland). Al_2O_3 balls were used as the friction pairs because Al_2O_3 is commonly used to make femoral heads in COM type artificial joints. Reciprocation friction mode was performed to evaluate the friction and wear of the DLC coating. The Al_2O_3 balls slid on the DLC coatings under 2 N with the sliding speed of 2.5 cm/s for 50,000 cycles. The sliding took place in air and pure water environment respectively and the wear track length was 6 mm. After the wear test, the bulk wear loss was calculated based on the cross-section profile of the wear track measured by the XP2 step profiler (AMBIOS, USA). The wear rate was normalized with respect to the applied load and sliding distance.

3. Results

3.1. The structure of the DLC coatings

The structure of DLC coatings was evaluated by Raman spectroscopy, as shown in Fig. 1. The Raman spectra of DLC coating consists of a D peak at about 1350 cm^{-1} and a G peak at about 1560 cm^{-1} . The integrated intensity ratio (I_D/I_G) was often used to reflect the content of sp^3 clusters [18]. Fig. 1 shows that hydrogenated HD1 and HD2 samples have lower I_D/I_G ratios than D3 sample, which indicates the hydrogenated DLC coatings (HD1 and HD2) have more sp^3 bonds than the hydrogen free D3 sample. For the hydrogenated DLC coatings, the sp^3 bonds consist of

Table 1
Properties of hydrogenated and hydrogen free DLC coatings.

Sample	HD1	HD2	D3
Coating thickness/ μm	2.5	2.2	2.2
Surface roughness(R_a)/nm	39.6	13.3	2.1
Hydrogen content	~23%	~40%	~0
Indentation hardness/GPa	32.7 ± 2.8	24.3 ± 1.5	54.4 ± 5.0
Indentation modulus/GPa	189.2 ± 11.5	132.3 ± 7.0	342.5 ± 26.8

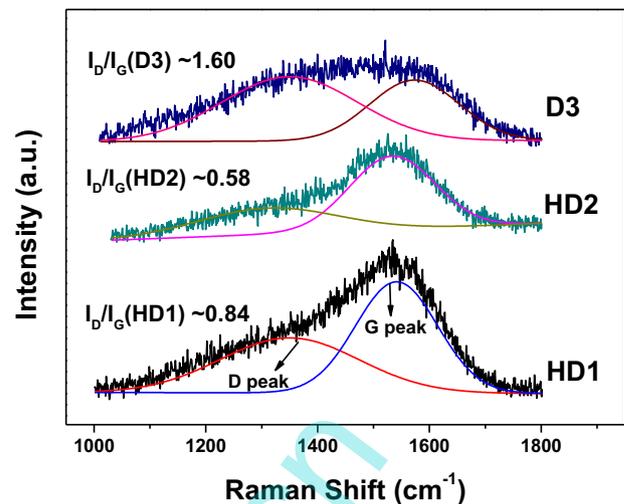


Fig. 1. Raman spectrum and I_D/I_G ratio of HD1, HD2 and D3 samples.

sp^3 -CC bonds and sp^3 -CH bonds. The sp^3 -CH bonds make no contribution to coating hardness, so the hardness of hydrogenated HD1 and HD2 is lower than that of hydrogen free D3 (Table 1).

The FTIR spectrum from 2500 cm^{-1} to 3500 cm^{-1} was used to analyze the -CH bonds in hydrogenated DLC coatings, as shown in Fig. 2. For HD1 sample, a large peak centering at about 2900 cm^{-1} reveals a strong absorption of saturated sp^3 -CH bonds vibration [19]. And a mild broad peak can be observed at about 3300 cm^{-1} , which may result from the vibration of the unsaturated sp^1 -CH bonds ($\text{C}=\text{CH}$) [20]. For HD2 sample, small absorption peaks at 2860 cm^{-1} , 2920 cm^{-1} and 2955 cm^{-1} can be observed indicating the saturated sp^3 -CH structure ($-\text{CH}_3$) in HD2. A strong broad peak between 3000 cm^{-1} and 3300 cm^{-1} also can be observed, which indicates the HD2 sample contains -CH bonds with unsaturated sp^2 ($\text{C}=\text{CH}_2$) and sp^1 structure [21]. Fig. 2 also shows that the HD1 sample has stronger peak around 2900 cm^{-1} than HD2 sample, which implies HD1 sample contains more saturated sp^3 -CH bonds than HD2. The HD2 sample shows stronger absorption peak ($3000 - 3300\text{ cm}^{-1}$) of unsaturated structure indicating HD2 has more unsaturated sp^2 & sp^1 -CH bonds compared with HD1. For hydrogen free D3 sample, no -CH absorption peaks can be observed because there is no hydrogen in the coating.

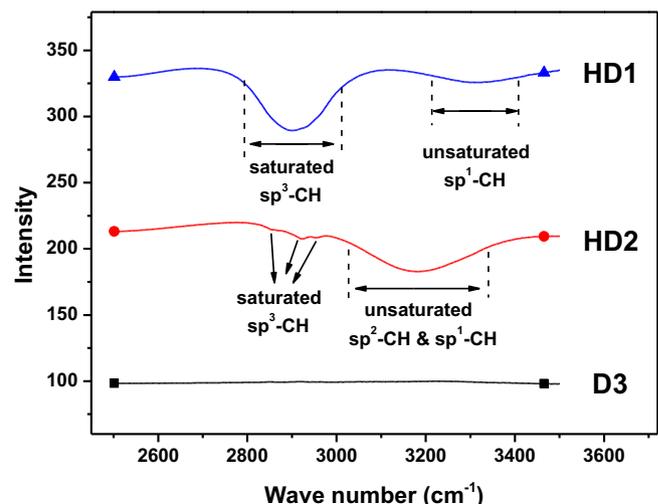


Fig. 2. FTIR spectrum of HD1, HD2 and D3 samples.

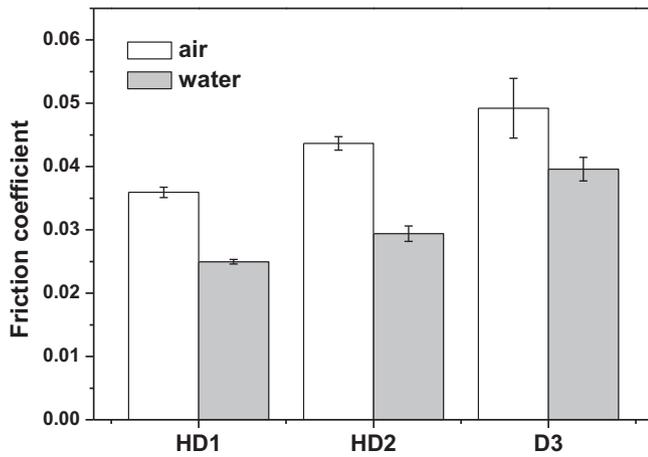


Fig. 3. Average friction coefficients of HD1, HD2 and D3 tested in air and water environment.

3.2. Friction of the DLC coatings

The tribological properties of the DLC coatings were tested against Al_2O_3 balls using reciprocation friction mode by a ball-on-disc tribometer in pure water and air, respectively. After ~ 3000 laps' friction, the friction coefficient became relatively stable. During steady wear stage, the friction coefficient at $\sim 10,000$, $\sim 25,000$ and $\sim 40,000$ laps was recorded to calculate the average friction coefficient. The average friction coefficients of the HD1, HD2 and D3 in air and water are shown in Fig. 3. In air environment, HD1 shows lower friction coefficient than HD2 and D3. D3 shows the highest friction coefficient. In water environment, HD1 still exhibits the lowest friction coefficient, and D3 exhibits the highest. All the three DLC samples show lower friction coefficients in water compared to those in air environment, which may result from the water lubrication effect for the sliding surfaces [22].

3.3. Wear of the DLC coatings

After the wear test, the cross-section profile of the wear track was measured at three different positions of the wear track. The average bulk wear rate was calculated according to the 3 measurements. The average wear rates of the DLC coatings in air and in pure water are shown in Fig. 4. In air environment, hydrogen free D3 sample, which has the highest hardness in three samples, shows the lowest wear rate. And hydrogenated HD2 sample, which has the lowest hardness, exhibits the

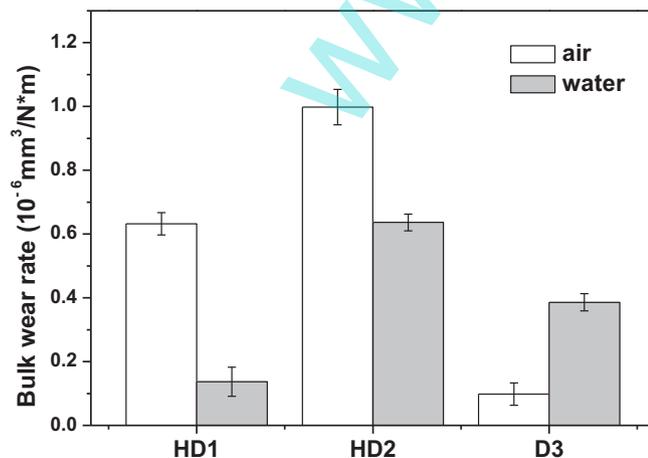


Fig. 4. Bulk wear rates of HD1, HD2 and D3 during the wear test in air and water environment.

highest wear rate. In water environment, the hydrogenated HD1 sample shows a lower wear rate than hydrogen free D3 sample although the hardness of HD1 is lower. However, the hydrogenated HD2 sample exhibits a higher wear rate than the hydrogen free D3 sample.

3.4. Raman spectra of the worn surfaces (wear tracks)

The structure of the wear tracks was evaluated by Raman spectra, as shown in Fig. 5. For HD1 (Fig. 5a) and D3 (Fig. 5c), the Raman spectra of

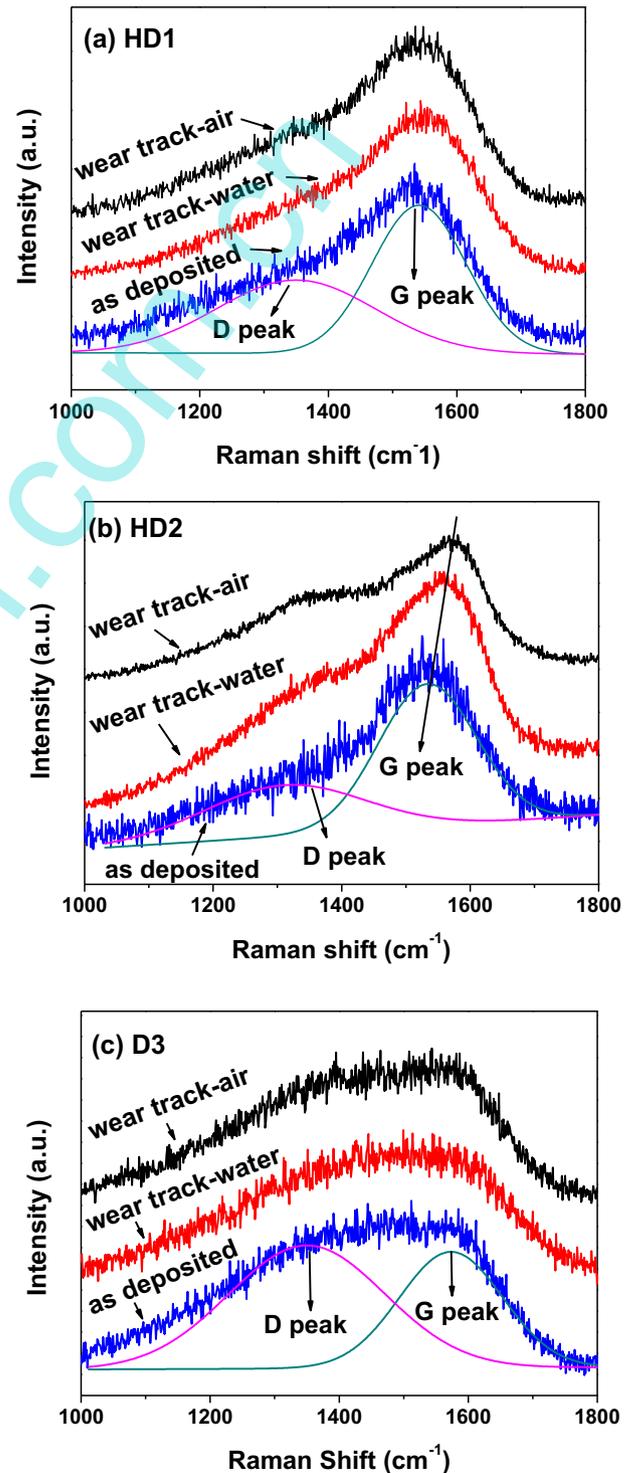


Fig. 5. Raman spectra of as deposited DLC films and wear tracks in air and in water. (a) HD1 sample, (b) HD2 sample, (c) D3 sample.

worn surfaces (wear in air and in water) are similar with the ones of as deposited surfaces. That indicates the structure of HD1 and D3 didn't transform under load and friction whatever in air or in water environment. For HD2 sample (Fig. 5b), the increasing intensity of D peak on worn surface (wear in air and in water) indicates an increasing content of carbon aromatic rings [23]. The G peak shifts toward a higher wave-number after the friction which reveals a decrease of sp^3 fraction in DLC film [24]. The increase of aromatic rings and decrease of sp^3 fraction mean a graphitization process. The worn surface on HD2 is graphitized to a softer structure whatever in air or in water environment, which indicates the structure with unsaturated sp^2 & sp^1 -CH bonds is unstable during friction process. In air environment, the graphitization degree of HD2 is higher than that in water environment because of the difference in friction surface temperature [12].

3.5. Analyses of the friction counterfaces

The optical morphologies of the Al_2O_3 counterfaces are shown in Fig. 6. In air environment, transfer layer is formed on the Al_2O_3 counterface when the Al_2O_3 ball slid against HD1 and HD2. For D3 sample, wear debris can be observed on the Al_2O_3 counterface as well. These wear products generated in air may provide solid lubrication for the sliding surfaces. Fig. 7 shows the Raman spectra of the wear products forming in air environment. All the wear products show a higher I_D/I_G ratio than the as deposited ones (Fig. 1), which reveals a graphitized structure of the wear products.

In water environment, wear products were invisible on all the Al_2O_3 counterfaces probably because water may restrain the formation of the transfer layer [25]. The solid lubrication in water environment may be insufficient and the sliding surface may be exposed directly to the water environment.

4. Discussion

In air environment, wear products may adhere on the Al_2O_3 counterfaces (Fig. 6) as solid lubricant during the sliding. Additionally, oxygen and vapor will take part in the tribochemical reaction and

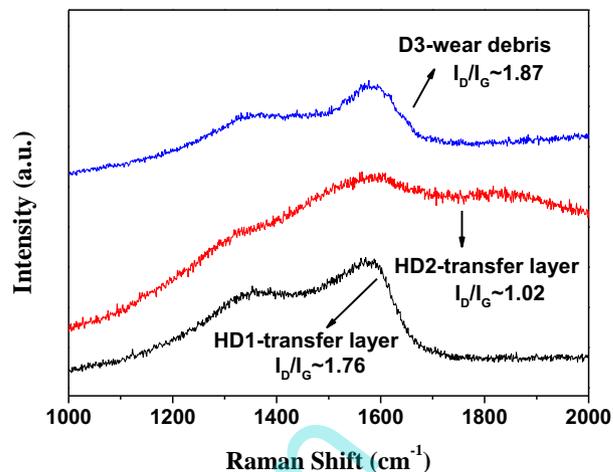


Fig. 7. Raman spectra of the wear products on Al_2O_3 counterfaces forming in air environment.

form oxygen containing groups on the surfaces of wear track and wear products. The hydrogen bonding interaction among these oxygen containing groups may increase the friction coefficient during the sliding [5]. For hydrogenated DLC films, hydrogen can terminate the carbon dangling bond and restrain the formation of oxygen containing groups. So compared with the hydrogen free DLC (D3), hydrogenated DLC (HD1 and HD2) show lower friction coefficient in air. Compared to HD1, HD2 contains more unsaturated -CH bonds, the unsaturated -CH bonds is unstable and easy to oxidate generating oxygen containing groups on the sliding surface, so the friction coefficient of HD2 is higher than HD1.

The wear of DLC film in air is related to solid lubrication, tribochemical reaction, film mechanical property and so on. In this paper, the hydrogenated HD1 and HD2 with lower hardness show larger wear rates, and the hydrogen free D3 with higher hardness shows lower wear rate. It reveals film hardness has important influence on

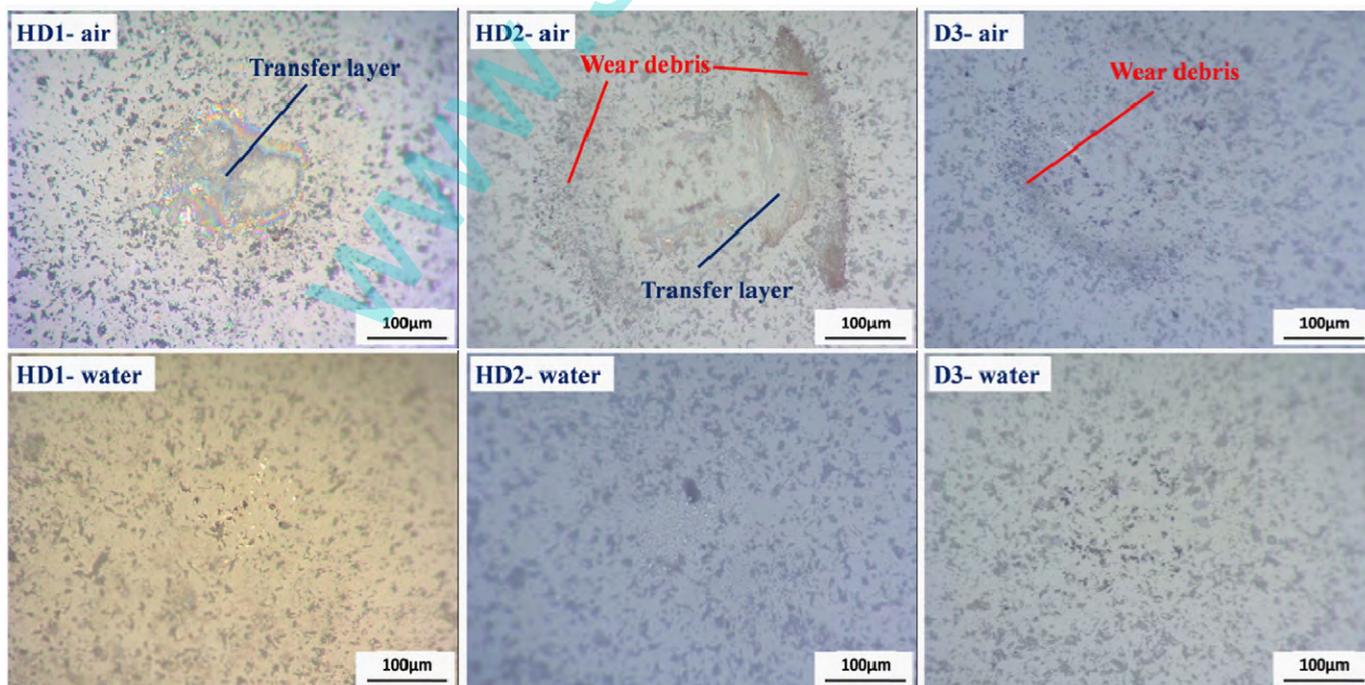


Fig. 6. OM images of the Al_2O_3 counterfaces in air and water environment.

the DLC wear in air. This result is in agreement with Ref. [12], in which the wear rate of the DLC coating decreases with increasing hardness.

In pure water environment, wear products can't gather on the Al_2O_3 counterfaces for all the samples (HD1, HD2 and D3), thus the effect of solid lubrication is weak, and the hydrogenated and hydrogen free surfaces will be exposed to the water environment. In that case, water may take part in the friction and provide lubrication for the sliding surfaces. For hydrogenated and hydrogen free DLC coatings, the lubrication film may consist of H_2O molecules formed by physical absorption and CH/COH groups generated by tribochemical reaction [26]. For hydrogenated HD1 sample, hydrogen may terminate the dangling carbon bond, restrain the tribochemical reaction and reduce the formation of oxygen containing groups. The interaction between -CH and H_2O or between -CH and Al_2O_3 is Van der Waals force. So the friction and wear of HD1 are relatively low in water environment. Hydrogenated HD2 sample also shows low friction coefficient in water environment, however, the low hardness and structure softening during the sliding induce a large wear rate. For D3 sample, without the termination of hydrogen, more oxygen containing groups will be produced on the sliding surface as lubrication film. The oxygen containing groups may induce hydrogen bond effect with water molecule [27]. The hydrogen bond effect is strong compared with the Van der Waals force. So the friction and wear of D3 in water environment is relatively high.

Previous references declare that hydrogenated DLC coating is susceptible to a high specific wear rate in water. However, the hydrogenated DLC coating mentioned in those articles are failed due to coating delamination [9,13,25,28]. In this paper, no catastrophic delamination happened during the friction test, the DLC coatings were worn away gradually layer by layer. In that case, hydrogenated DLC coatings with saturated structure may exhibit good wear resistance in water environment.

5. Conclusions

Hydrogenated and hydrogen free DLC coatings were prepared on the CoCrMo alloy. In air environment, DLC coatings slide against Al_2O_3 balls under solid lubrication condition, the wear rate is mainly related to coating hardness. The hydrogen lowers the coating hardness and brings more DLC wear. In water environment, DLC coatings slide against Al_2O_3 balls under water lubrication condition. In that case, the hydrogen in hydrogenated DLC coating become vital to influence the wear. The hydrogenated DLC coating with saturated sp^3 -CH bonds produces the least friction and wear, even though its hardness is lower. The hydrogen free DLC coating may generate relatively high friction and wear without H termination in water environment. The hydrogenated DLC coating with unsaturated sp^2 & sp^1 -CH bond reveals an unstable structure, which is easily transformed to a softer graphite phase and produce a high wear rate whatever in air or in water environment.

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