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# Superlubricity of the DLC films-related friction system at elevated temperature

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Superlubricity is defined as a sliding regime in which friction or resistance to sliding almost vanishes. While there are a number of superlubricity, providing a high temperature superlubricity remains a challenge. Here we present a high temperature superlubricity achieved from the Diamond like carbon (DLC) films friction system. Superlubricity is found about 0.008 for more than 100,000 seconds at the steady state at the temperature of 600°C due to the formation of the self-generated lubricious composite oxides of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> at the contact surfaces through tribochemistry reaction during the running-in process. We propose a superlubricity system based on the repulsive electrostatic forces between the self-generated composite oxides due to high temperature oxidation reaction and the shielding action of hydrogen at the contact surface, which is seem to be a reasonable explanation for super low friction at the elevated temperature.

## 1. Introduction

Diamond like carbon (DLC) films exhibit attractive high hardness, high chemical stability, high wear resistance and low coefficient of friction, which makes DLC films as good candidates for the tribological applications.<sup>1,2</sup> Many researches have been devoted to investigate the tribological properties of DLC

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films.<sup>3,4</sup> However, the application of DLC films in industry is limited by high internal stress and low thermal stability in the tribology fields.<sup>5, 6</sup> The graphitization temperature of carbon-related material films is around 200°C for amorphous carbon films and 300°C for DLC films.<sup>7</sup> During sliding, DLC films are delaminated from the steel substrate and oxidized with oxygen or water molecular in ambient air under high friction heat and environmental temperature simultaneously, which makes the performance of DLC films deterioration in the tribological properties. Moreover, after the escape of DLC films, the steel substrate is exposed and oxidized in ambient air at elevated temperature.<sup>8</sup> There existing physical, chemical reaction and structural changes in the films during sliding, and products of these chemical reactions and changes affecting strongly the tribological properties of the friction system. Therefore, the friction system of the carbon-related films exhibits an unexpected high friction and even causes the failure of parts, but the reasons have not been clarified clearly yet. Many studies have been investigated the tribological properties of DLC films at room temperature or below 500°C in ambient air.<sup>9-11</sup> With the rapid development of industry, DLC films are extendable used to high operating temperature like above 500°C conditions in engineering application. However, a series of problems arises and should be discussed: 1) What is the oxidization temperature and oxidization mechanism of DLC films? 2) And what is relation with the tribological properties of the friction system at elevated temperature? 3) Is it possible to obtain low friction and how to improve the tribological properties of carbon-related material films under high temperature?

Therefore, it is necessary to investigate the tribological properties and clarify its friction mechanism of the DLC-related friction system at elevated temperature. In this paper, the tribological properties of the DLC-related friction system are investigated at the temperatures of 25°C, 100°C, 200°C, 300°C, 400°C, 500°C and 600°C respectively in ambient air, and the further understanding of the mechanism responsible for the antifriction behavior and high wear-resistance of the DLC-related friction system are also clarified.

## 2. Experimental details

DLC films were deposited on AISI H13 steel disc and 440C steel balls in the r.f. capacitive coupled plasma enhanced chemical vapor deposition system, respectively. The steel substrates were carefully polished and then cleaned ultrasonically in acetone for 10 minutes. Prior to the deposition of DLC films, the steel and ball substrates were etched with Ar ion to remove the native oxides and contamination. And then a thin layer of Si films as the transition layer was deposited to enhance the bonding strength before the deposition of DLC films. The gas pressure is 1.3 Pa and r.f. bias voltage is 500 V during the films deposition. The thickness of the films is about 1  $\mu\text{m}$ .

The friction and wear tests were performed by a ball on disk rotating-type tribometer to evaluate the tribological properties of DLC films-related friction system in ambient air from room temperature to 600°C. The ball and disc were both cleaned with acetone for 10 min and blown using dry nitrogen prior to the experiment for each friction test. The rotating disk was heated to the set temperatures, which was kept as the constant value during the tribotests. The

static ball was not heated and contacted with disc until the tribotest starting. The environmental conditions are controlled in order to ensure the same friction conditions for all friction and wear tests. The friction and wear tests are run three times for each friction pair. The new disc and ball are used for each test. The ball slides over H13 steel disk at the speed of 0.05 m/s and normal load of 2 N. The initial maximum Hertz contact pressure is approximate 0.34 GPa assuming that ball is contacted directly with disc. The hardness of H13 steel substrate is about 61 HRC. The worn surface topography of the friction pair was observed by 3D non-contact optical profiler. The worn surface and the micro structure characteristics of the friction pair were investigated by Raman spectroscopy (Renishaw Ramanscope) using a 632.8 nm He–Ne laser excitation source with a resolution of 1–2  $\text{cm}^{-1}$ .

### 3. Results and discussion

Fig. 1 shows COF of the friction pair with sliding time in ambient air under different temperatures. Tables 1 and 2 show COF of the friction pair at the initial and stable stage, respectively. At room temperature, COF is 0.164 at the initial stage and then decreases, finally reaches the stable average value of 0.127. At the temperature of 100°C, COF is 0.117 at the initial stage and then decreases to 0.01 suddenly and keeps this value about 1000 seconds, finally increases slowly with the increase of sliding time. Average COF is 0.067 at the temperature of 100°C. For 200°C, COF is 0.048 at the initial stage and then decreases gradually to 0.002, which exhibits super low friction. After 1000 seconds, COF increases slowly to around 0.018 of the average value. At the

temperature of 300°C, COF is 0.017 at the initial stage and then increases fast to 0.54. At the temperature of 400°C, COF is high as 0.79 at the initial stage, and then COF fluctuates during the friction test. At the temperature of 500°C, COF is 0.352 at the initial stage and then increases suddenly to 0.82. Fig. 2 shows COF of the friction pair in ambient air at the temperature of 600°C. The curve of COF is smooth until the end of friction and wear test. COF is 0.42 at the initial stage, and then decreases to 0.008 of the stable value. From room temperature to 200°C, COF decreases firstly to the minimum value and then increases slightly to the stable value with sliding time. The curve of COF is smooth. However, the shape of COF curve is difference and COF fluctuates strongly above 200°C. COF increases to high value firstly and then decreases. At the initial stage, COF decreases from 0.164 to 0.017 from 25°C to 300°C. However, COF is as high as 0.79 at temperature of 400°C. Average COF decreases from 0.127 to 0.018 with increase of temperatures from 25°C to 200°C. However, COF are high and 0.376, 0.228 and 0.539 from 300°C to 500°C, respectively, as shown in Table 2.

According to the experiment results, we did the friction and wear test of the DLC-related friction system at the temperature of 700°C to understand its friction behavior. Fig.3 shows COF of the friction pair at the temperature of 700°C. COF is about 0.25 at the initial stage and COF decreases suddenly within few seconds, and then COF increases with the increase of the sliding time. At the temperature of 700°C the friction system doesn't exhibit the superlubricity like that of the temperature of 600°C in spite of low friction.

Fig.4 shows the worn surface topography of the disc under different temperatures. It is shown that there is invisible wear scar on the disc from room temperature to 200°C. At the temperatures of 300 °C and 400 °C, there occurs groove and DLC films are worn away partially on the disc surface. There is some black material in the wear scar at the temperature of 300°C. However, black material vanish and the groove becomes deep even DLC films are worn out partially at the temperature of 400°C. DLC films are escaped entirely from the disc surface and there are deep groove on the disc surface and a lot of black wear debris on the edge of wear scar at the temperature of 500°C. At the temperature of 600°C, DLC films are also oxidized on the disc surface and there are the deep grooves on the wear scar of the disc surface. COF is 0.008 at the stable stage at the temperature of 600°C and finally COF increases, therefore, it is necessary to investigate whether DLC films were worn out or not. Fig.5 shows surface topography of ball after the friction test at the temperature of 600°C. It seems to be presumable at the initial stage that there are DLC films on the ball, which makes COF showing super low friction for the tribological system at the temperature of 600°C. At the end of the friction tests, COF increases when DLC films are worn out partially on the ball. The wear performance is consistent with the friction behavior of the friction pair.

The experimental results show that the tribological properties of self-mated DLC films are closely related with temperature, which means the initial chemical state of the heating disc surface. The tribological process of the

friction system is very complicated because there are many factors such as oxidation and tribochemistry reaction in open air especially in high temperature. Therefore, it is necessary to investigate and analyze surface topography and microstructure of the friction interface under different temperatures.

### 3.2 Raman spectroscopy for characterizing the worn surface structure

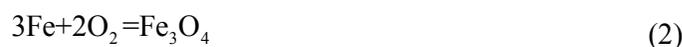
For a good understanding of the temperature influencing the tribological process, the structure changes of the friction pair surface will be investigated after the friction tests. The worn surface microstructures of the disc and ball were measured by Raman spectroscopy. Fig.6 shows Raman spectroscopy of the friction pair. Temperature influenced the physical and chemical properties of the friction pair surface because there are tribochemistry reactions during high temperature friction tests.<sup>12, 13</sup> From room temperature to 200°C, Raman spectroscopies of DLC films on the ball are almost the same to as-is DLC films. There is a little different in the band around 1380  $\text{cm}^{-1}$  at the temperatures of 100°C and 200°C, which means there is slightly graphitization in DLC films. At the temperature of 300°C, there are two obvious 1374  $\text{cm}^{-1}$  and 1563  $\text{cm}^{-1}$  band, which is D and G band of DLC films respectively. There is a new band of 669  $\text{cm}^{-1}$ , which is typical peak of  $\text{Fe}_3\text{O}_4$ .<sup>14</sup> This band becomes obvious and strong at the temperature of 400 °C. In addition to, there is a band of 513  $\text{cm}^{-1}$ , which is another typical band of  $\text{Fe}_3\text{O}_4$ . D peak shifts to low wave number and G peak shifts to high wave number in DLC films, which means the presence of the graphitization. The phenomena become obvious with increase of temperature.

This means the graphitization tribochemistry reaction simultaneously during running-in progress at the temperatures of 300°C and 400°C. At the temperature of 500°C, the peak of 1568  $\text{cm}^{-1}$  disappears, however, there are the bands of 224  $\text{cm}^{-1}$ , 290  $\text{cm}^{-1}$ , 408  $\text{cm}^{-1}$  and 499  $\text{cm}^{-1}$ , which are all typical band of  $\alpha\text{-Fe}_2\text{O}_3$ . The peak of 1343  $\text{cm}^{-1}$  shifts to 1315  $\text{cm}^{-1}$ , which is not the peak of DLC films but the typical peak of  $\alpha\text{-Fe}_2\text{O}_3$  because there were no DLC films on the ball after the friction tests. And the peak of 670  $\text{cm}^{-1}$  shifts to 661  $\text{cm}^{-1}$ , which is the typical band of  $\text{SiO}_2$ . Therefore, the wear debris is  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . At the temperature of 600°C, there are 1340  $\text{cm}^{-1}$  and 1588  $\text{cm}^{-1}$  band, which are typical peaks of  $\gamma\text{-Fe}_2\text{O}_3$ . The band of 661  $\text{cm}^{-1}$  shifts to 664  $\text{cm}^{-1}$ , which is typical peak of  $\text{SiO}_2$ . Therefore, the wear debris is  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . For the worn surface of the disc, there is a little difference from that of ball. There are DLC films on the worn surface from ambient temperature to 400°C, as shown in Fig.3. At the temperature of 500 °C, there are some bands of 226  $\text{cm}^{-1}$ , 293  $\text{cm}^{-1}$ , 413  $\text{cm}^{-1}$ , 502  $\text{cm}^{-1}$ , 614  $\text{cm}^{-1}$ , 663  $\text{cm}^{-1}$  and 1526  $\text{cm}^{-1}$ , which are typical bands of  $\alpha\text{-Fe}_2\text{O}_3$ . At the temperature of 600°C, there is a band of 656  $\text{cm}^{-1}$ , which is peak of  $\text{SiO}_2$ . It means that the wear debris is mainly  $\text{SiO}_2$  on the disc surface.

### 3.3 The friction mechanism (under different temperatures)

The experimental results show that DLC films and the steel substrate are oxidized by oxygen or water molecular during the tribological process. However, not all chemical reaction products may improve the tribological properties of the friction system. Involved in the tribological process must be characterized carefully. Raman spectroscopy results fit the tribological experiment results. The

tribochemistry reactions in the tribological system took place unavoidable under higher temperature and friction heating conditions. According to the friction and wear experimental results and Raman measurement results and analysis of the friction pair, the environmental temperature and the frictional heat play different roles in the tribological properties of the friction pair due to the oxidation of the friction pair contact surface in open air. The possible oxidation reactions on the friction are listed.



Fe may be oxidized to  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and FeO respectively at the range temperature of 300°C-500°C. However, the oxidation products are depend to the friction condition.  $\text{Fe}_3\text{O}_4$  is easily generated, however, under the conditions of the sufficient oxygen,  $\text{Fe}_3\text{O}_4$  and FeO are oxidized completely to  $\alpha\text{-Fe}_2\text{O}_3$ . The oxidation reactions between Fe, C and O affect the reduction or even determine the friction behavior of the friction pair. When the temperature is below 200°C, the friction takes place mainly between DLC films and COF is low and stable since the solid lubrication of DLC films. When the temperature increase to 300°C, there is graphitization in DLC films before the friction and wear test, resulting in a lower COF. During the sliding process, DLC films were worn out, and the steel substrate was oxidized by oxygen under high temperature and

pressure. The products of the oxidation reaction are mainly  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , which makes COF increasing suddenly. However, there is few DLC films on the worn surface, COF is not high. But the disc persist carbon, can play a role in lubrication, low coefficient of friction. At the temperature of  $400^\circ\text{C}$ , before the friction test, COF is very high due to the loose carbon films, and then carbon films are worn out totally, the fresh surface is exposed and oxidized by oxygen. The products of the oxidation reaction are mainly  $\text{Fe}_3\text{O}_4$  due to the possible

oxidation-reduction reactions:  $\frac{1}{3}\text{CO} + \text{Fe}_2\text{O}_3 = \frac{2}{3}\text{Fe}_3\text{O}_4 + \frac{1}{3}\text{CO}_2$ . Therefore, COF is

lower than that of the friction pair because COF of  $\text{Fe}_2\text{O}_3$  is lower than  $\text{Fe}_3\text{O}_4$  under the same friction conditions. For the same reason, COF of the friction system at the temperature of  $500^\circ\text{C}$  is lower than that at the temperature of  $400^\circ\text{C}$ . When the temperature increasing to  $600^\circ\text{C}$ , DLC films are oxidized and the steel disc is evaporated and oxidized, redox reactions do not occur at the initial stage. And  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are transformed to  $\gamma\text{-Fe}_2\text{O}_3$  around  $600^\circ\text{C}$ . And the transformation of the  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  phase increases along with the increase of temperature. The transformation of  $\gamma\text{-Fe}_2\text{O}_3$  was complete above  $500^\circ\text{C}$ .<sup>[15]</sup> It is understood that if the synthesis of  $\gamma\text{-Fe}_2\text{O}_3$  could be taken through the conversion of a naturally occurring iron ( $\alpha\text{-Fe}_2\text{O}_3$ ), an economic route to the synthesis of this important ferrite and superlubricity could be achieved. And the intermediate layer of Si films can be oxidized to  $\text{SiO}_2$  by oxygen and further oxidized by water molecular in ambient air (as shown in equation 4 and 5) under high temperature and friction heating environment simultaneous during the

friction tests. It can be concluded that the tribochemical reaction between SiO<sub>2</sub> and water can produce a silica layer that deposits on the worn region of the disc during the running-in process. These tribochemical reaction products maybe have an effect on the superlubricity. Especially, it indicates that the silica layer produced by the tribochemical reaction can provide a low friction coefficient, which is in accordance with the friction result of ceramic material under water lubrication [16, 17].



From the experimental results, it is found that the environmental temperature influences strongly the tribological properties of the friction system. There is different microstructure of the disc surface due to the tribochemistry reaction under different temperatures. Moreover, the friction heat promotes the tribochemistry reaction, especially in high temperature. According to the preparation of DLC films, the first layer is a transition layer of Si films on H13 steel substrate and the outermost layer is DLC films. Fig.6 shows the schematic diagram of the friction pair. As a function of time, the geometry and the material composition are varied and analyzed systematically on the basis of temperature during the tribological process. At ambient temperature, the friction generates between DLC films and DLC films, thus COF is low and stable. From 100°C to 300°C, the graphitization in DLC films appears and becomes obvious with the increase of temperature. The contact pair is DLC films/DLC films at initial stage. The initial COF decreases from 0.164 to 0.017 from ambient temperature to

300°C. The graphitization of DLC films become more severe at the temperature of 300°C, therefore, the initial COF is as low as 0.017.<sup>18</sup> However, the structures of DLC films become worse before the friction tests, even DLC films are worn away and the steel substrate is oxidized by oxygen and water molecule, which causes high COF at the stable stage. Above 300°C, it is conceivable that the molecular hydrogen is probably to diffuse and even escape from DLC films. Therefore, the films become loose and rough. When the temperature increases further, the films are oxidized by oxygen and water molecular after the evaporation of DLC films in open air. The iron oxides, which are confirmed by Raman spectroscopy, produced through tribochemistry reactions after the exposure of the steel substrate in ambient air. According to the Raman spectroscopy results, it is deduced that the contact pair is DLC/DLC films and Fe<sub>3</sub>O<sub>4</sub> at the initial stage at the temperatures of 400°C. Before the friction test, the iron atom is oxidized to Fe<sub>3</sub>O<sub>4</sub>, thus the surface roughness became high, which causes the initial COF as high as 0.789 even there is DLC films on the disc. At the temperature of 500°C, DLC films on the disc were escaped completely from the steel substrate and it was oxidized in open air, thus the contact pair is DLC films and α-Fe<sub>2</sub>O<sub>3</sub> at the initial stage, which causes also high initial COF. COF at the temperatures of 500°C is higher than that of 400°C because the tribological property of Fe<sub>3</sub>O<sub>4</sub> is better than that of α-Fe<sub>2</sub>O<sub>3</sub>.<sup>19</sup> There also occur tribochemistry reaction and products are α-Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the ball,<sup>20</sup> which makes high and stable COF. At the temperature of 600°C, DLC films on the disc were also escaped completely. The transition layer of Si films and

the steel substrate were oxidized, thus the contact pair is iron oxide and SiO<sub>2</sub>. It is deduced there is  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the disc at the initial stage according to Raman spectroscopy. There is  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> on the disc at the temperature of 600°C. The contact pair is DLC films and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> resulting in high COF at the initial stage. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> has relative low ductile <sup>21</sup> and SiO<sub>2</sub> exhibits high hardness and strengthen, which makes the composite oxide possessing high ductility and strengthen simultaneously.

From ambient temperature to 200°C, COF is stable during the friction tests, and the structure of DLC films is almost the same as that of as-is DLC films. It is well known that the graphitization of DLC films is occurred around 200°C owing to the dehydrogenation of DLC films and the transformation of sp<sup>3</sup>-bonded carbon atoms into sp<sup>2</sup>-bonded atoms in open air. The graphitization of DLC films is considered firstly. It is concluded that the graphitization of DLC films controls the tribological properties of the friction pair at low temperature. Consequently, the tribological properties of DLC films are affected strongly when the friction pair is subjected simultaneously to thermal and friction heat above 300°C. When the temperature increasing further, DLC films and the steel substrate are oxidized with oxygen and water vapor through oxidation and tribochemical reaction under high contact pressure and temperature conditions. There is iron oxide at the temperatures of 300°C and 400°C, resulting in high COF. At the temperature of 500°C,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is produced on the contact surface, thus COF is also high.

At the temperature of 600 °C, there are DLC films on the ball and the composite

oxide of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$  on the disc before the friction test through high temperature oxidation reaction, thus the contact pair is DLC films/ $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . Erdemir built a crystal chemistry model which related friction coefficients of solid oxides with their ionic potentials.<sup>22, 23</sup> The high-temperature COF of solid oxides (such as  $\text{V}_2\text{O}_5$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{B}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZrO}_2$ , etc.) varies with component from 0.1 to 1. The certain solid oxides are capable of affording fairly low friction coefficients (i.e., 0.1-0.3) to sliding contact interfaces at elevated temperatures and hence referred to as lubricious oxides. According to the previous studies, it seems that it is difficult to achieve superlubricity in the pure solid oxides tribological system. In the present work, at the temperature of  $600^\circ\text{C}$ , at the end of the friction and wear test DLC films on the ball are worn out and on the worn surface there are the composite oxides of  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$ , which makes high COF, as shown in Fig.2. However, according to the experimental results and analysis, the contact pair is DLC films and  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$  at the initial and steady stage, which makes low and stable COF. The two surfaces are in true rough asperity contact when sliding begins, COF is high. After a period of sliding time,  $\gamma\text{-Fe}_2\text{O}_3$  are melt under friction and environment heating and formed to a very thin silica layer during sliding, this may separate the contact surface and ensure that the friction force will be low and that sliding will proceed smoothly. The self-generated composite oxide of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$  on the surface does not necessarily have the same properties of normal lubricants. In the self-generated composite oxide, the soft  $\gamma\text{-Fe}_2\text{O}_3$  is connected with high strengthen  $\text{SiO}_2$  through covalent grafting to form the

strong structure under high temperature, which weak electrostatic interactions (whenever such type of interactions exist). The  $\gamma\text{-Fe}_2\text{O}_3$  acts as a soft solid lubricant between the contact surfaces. The silica layer plays an important role in the friction behavior of self-generated composite oxide, the adsorption of substances onto the contact surface and the low friction. Therefore, the contact pair of DLC films/the self-generated composite oxide exhibits super low friction at the temperature of 600°C. At the end of the friction and wear test, DLC films are worn out and the intermediate layer of Si films and the steel substrate are oxidized, after the friction and wear test the contact friction pair is supposed mainly to  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$  and  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$ , even  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$  and  $\text{SiO}_2$ , which causes high initial COF at the end of the friction and wear test and the temperatures of 600°C.

Hydrogen in DLC films plays a role in the shielding action in DLC films. The synergism of the passive of DLC films on the ball and the self-generated composite oxides on the contact surface are beneficial to super low friction at the temperature of 600°C. The presence of di-hydrated carbon atoms on DLC films surfaces is expected to provide excellent shielding or a higher degree of chemical passivation, thus lower friction. The elimination of the possibility of strong covalent and  $\pi\text{-}\pi^*$  interactions at sliding DLC interfaces, plus excellent shielding of carbon atoms by di-hydration are the major reasons for the superlubricity of DLC films.<sup>1</sup> Such repulsive forces at sliding interface may counter-act and or -balance the weak van der Waals attractions. Salonen et al using molecular dynamics computer simulations show that the buildup of a high

hydrogen content at the surface leads to a shielding of carbon atoms by the hydrogen and hence a decrease in the cross section of collisions with carbon atoms, namely a shielding of carbon by the hydrogen atoms.<sup>24</sup> The high H content leads to the shielding of carbon atoms from the adhesion of other material element, and thus a decrease of roughly an order of magnitude in COF. Hence our experimental results strongly indicate that the shielding effect described in this paper explains the experimental drop in COF. The shielding effect has implications for the superlubricity development. Overall, these experiments demonstrate that hydrogen on sliding carbon surfaces may have significant effects on the frictional behavior of DLC films.

The results show that DLC films on the ball and the self-generated composite oxides of  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$  on the disc through tribochemistry reaction simultaneously are beneficial to achieve the superlubricity of the friction system at the temperature of 600°C. The mechanism of superlubricity is supposed to the shielding action of hydrogen in DLC films and the self-generated composite oxide of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$  on the contact surface according to our experimental results and other researchers' theory.

#### **4. Conclusions**

In the present work, the influence of temperature on the tribological properties of self-mated DLC films is investigated in ambient air from ambient temperature to 600°C and the friction mechanism of DLC films is discussed on the basis of the experimental results and Raman spectroscopy analyses. The

following conclusions can be drawn:

(1) At the initial stage, COF decreases from 0.164 to 0.017 from ambient temperature to 300°C, however, COF is high above 300 °C. At the stable stage, average COF decreases from 0.127 to 0.018 from ambient temperature to 200°C and is not regular above 200°C.

(2) The friction mechanism of the friction system is the graphitization at low temperature and the oxidation reaction at elevated temperature.

(3) COF is as super low as 0.008, which exhibits super low friction at temperature of 600°C.

(4) Super low friction mechanism is the synergism of the shielding action of hydrogen in DLC films and the self-generated composite oxide of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the contact surface.

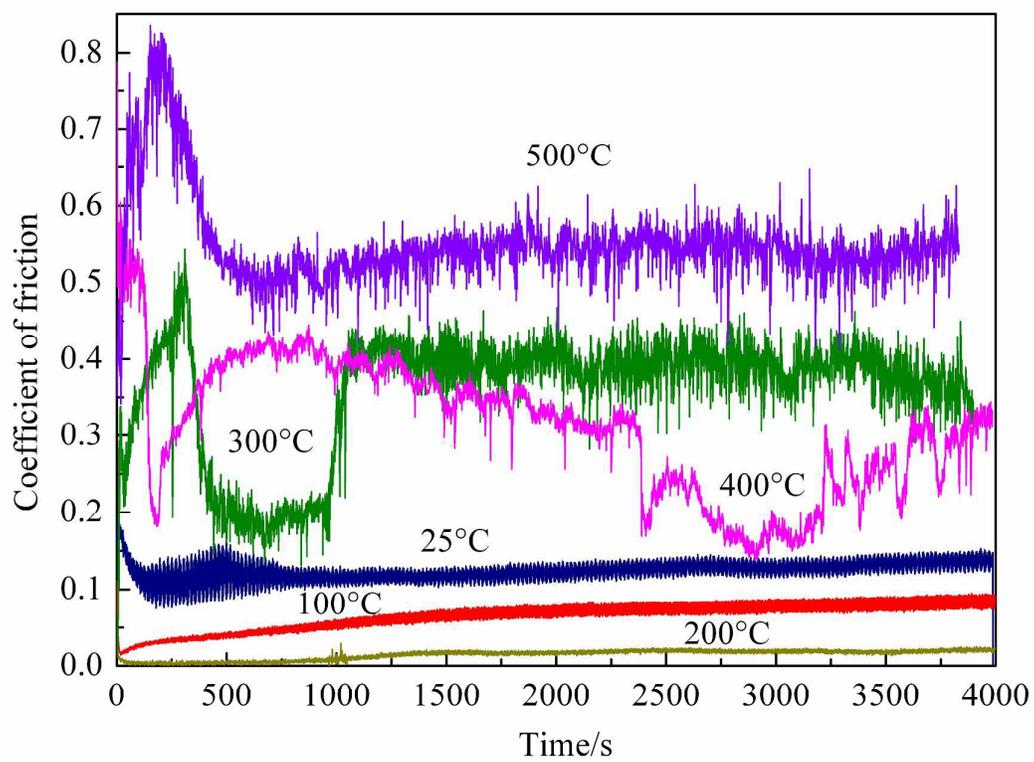
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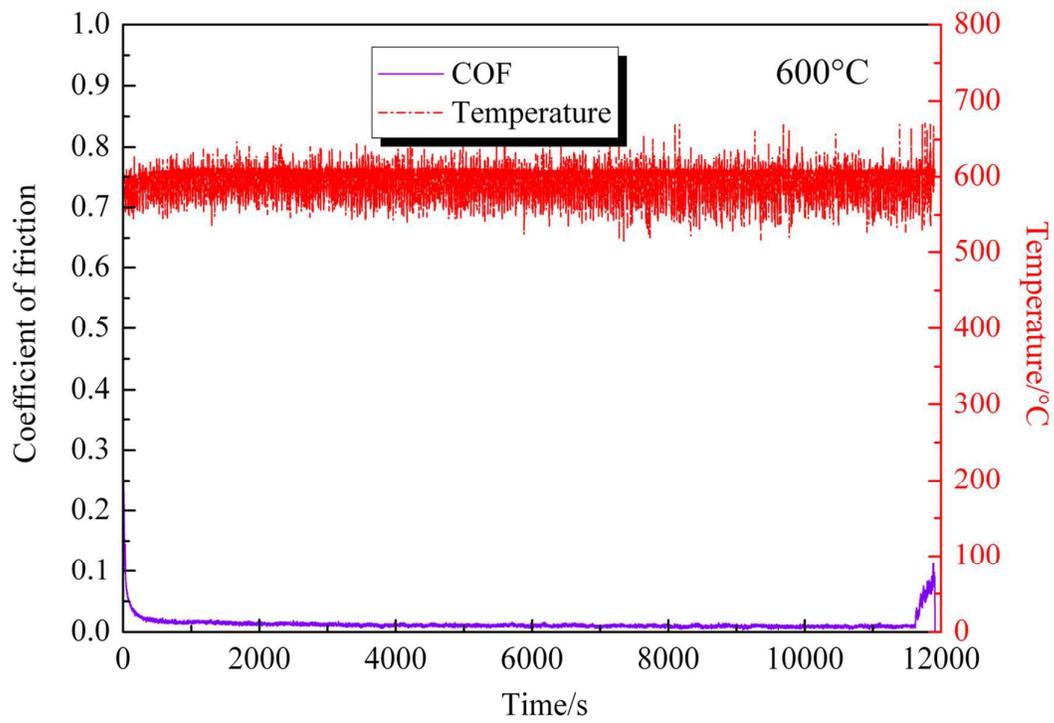
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**Fig.1** COF of the friction pair versus sliding time under different temperatures



**Fig.2** COF of the friction pair versus sliding time at the temperature of 600°C

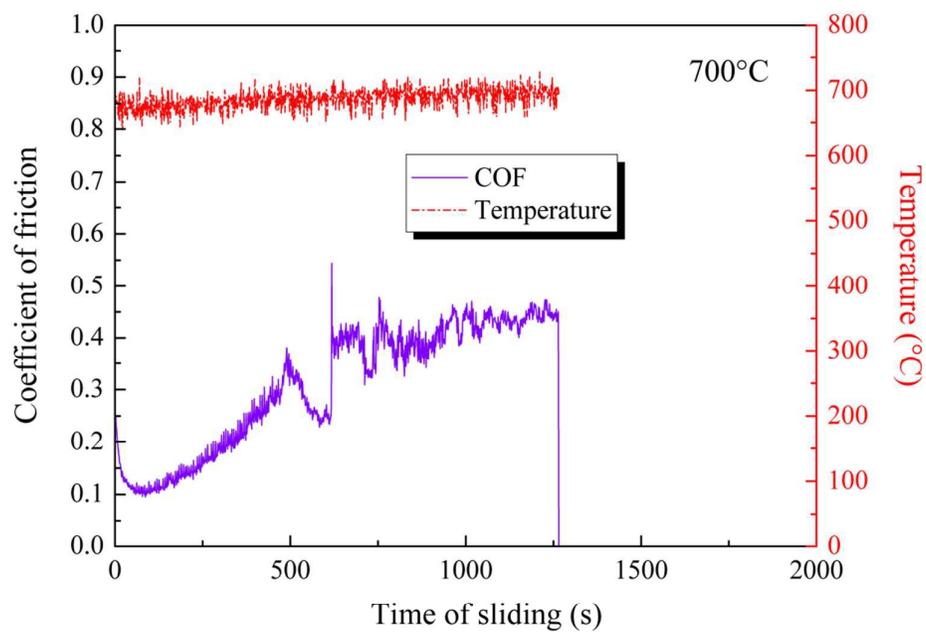
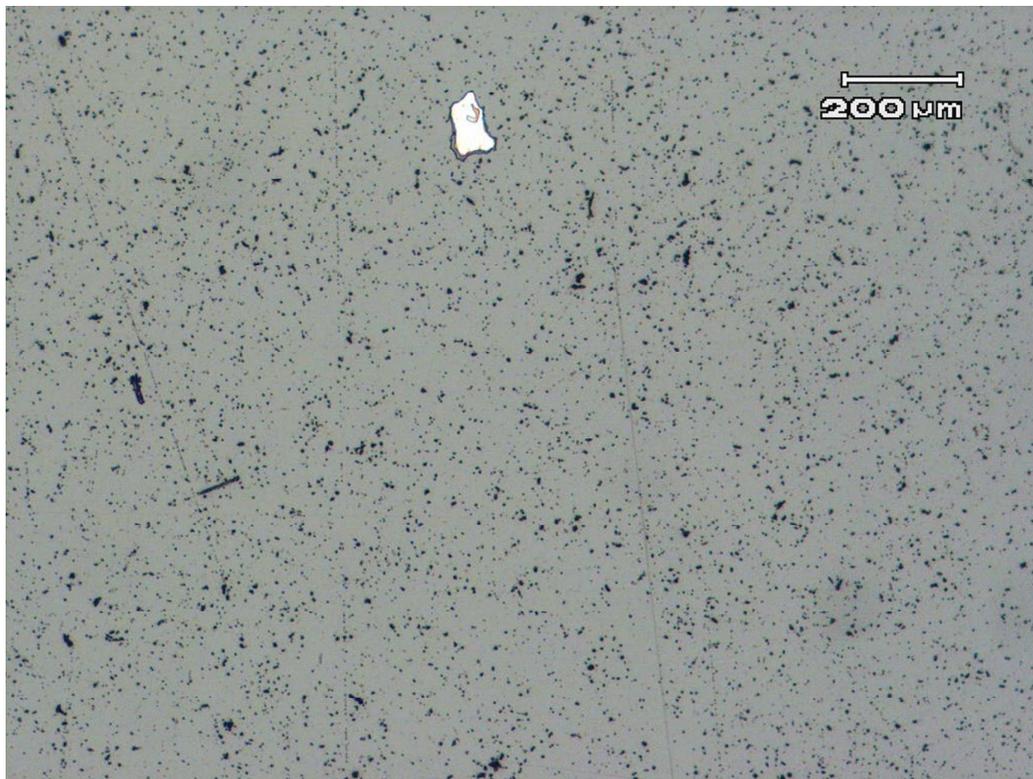
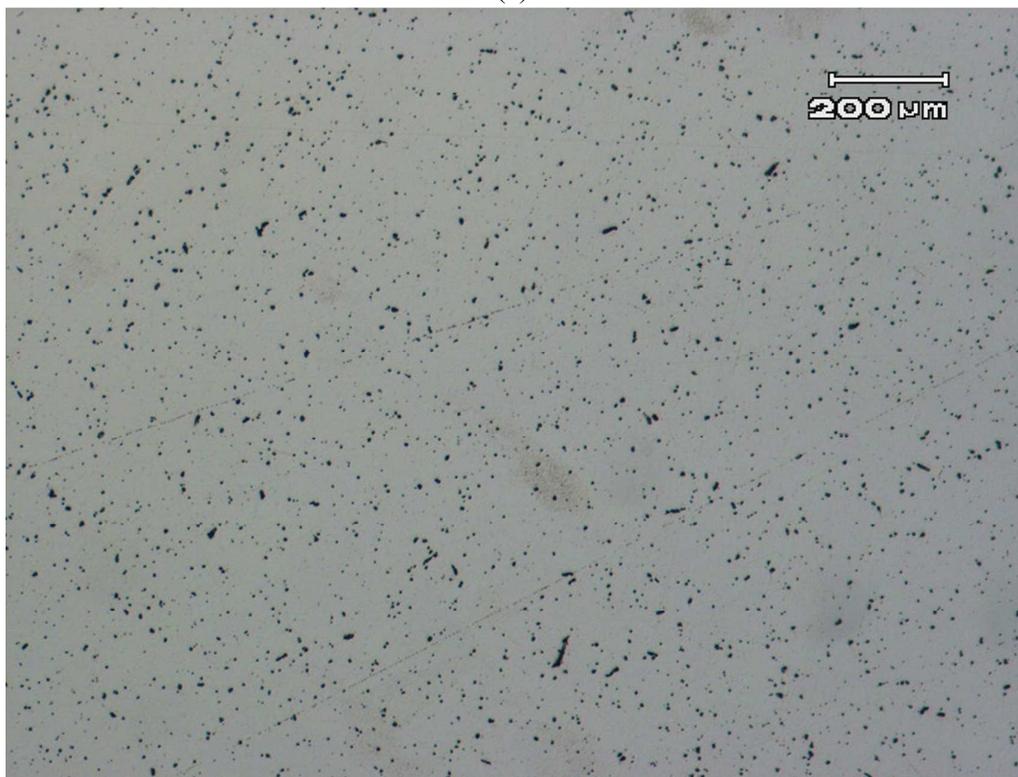


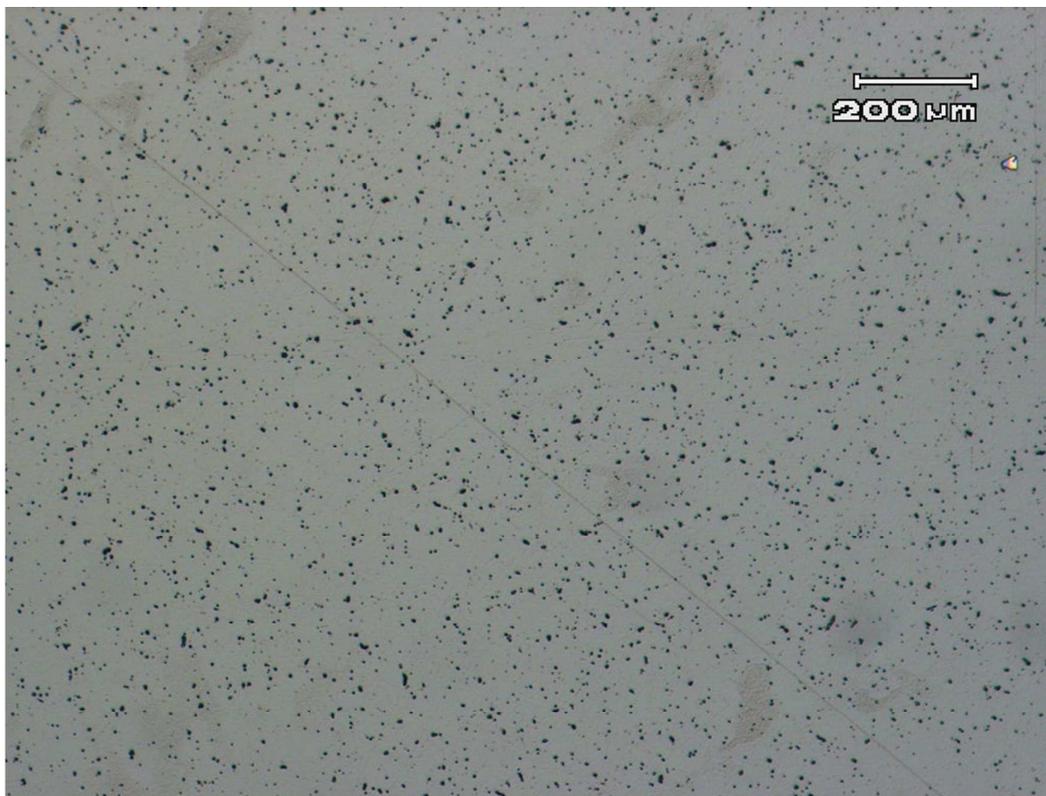
Fig.3 COF of the friction pair at the temperature of 700°C



(a) 25 °C



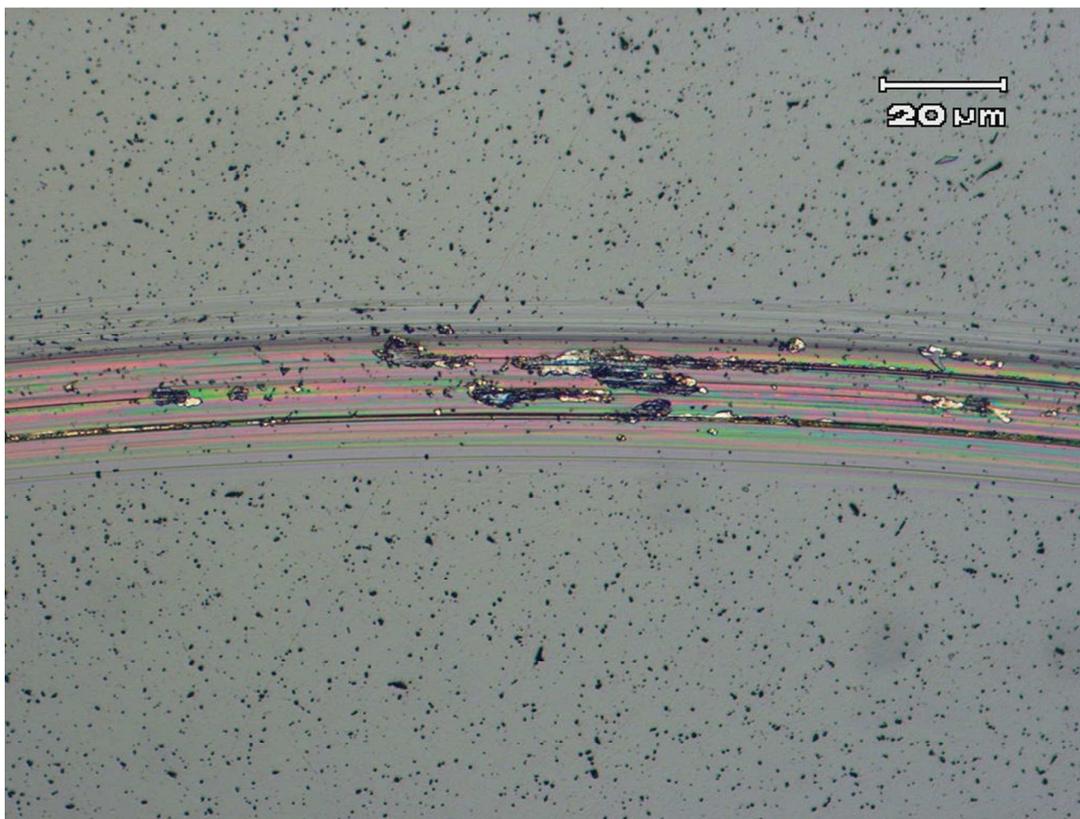
(b) 100 °C



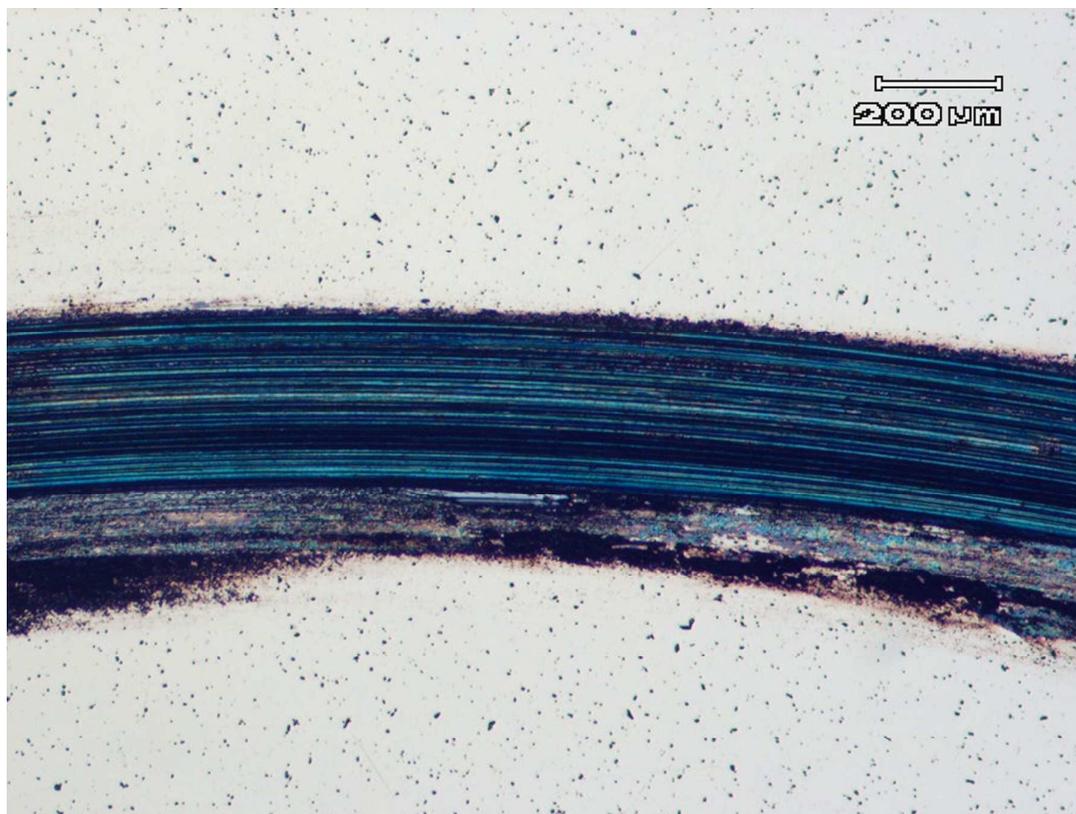
(c) 200 °C



(d) 300 °C



(e) 400 °C



(f) 500 °C

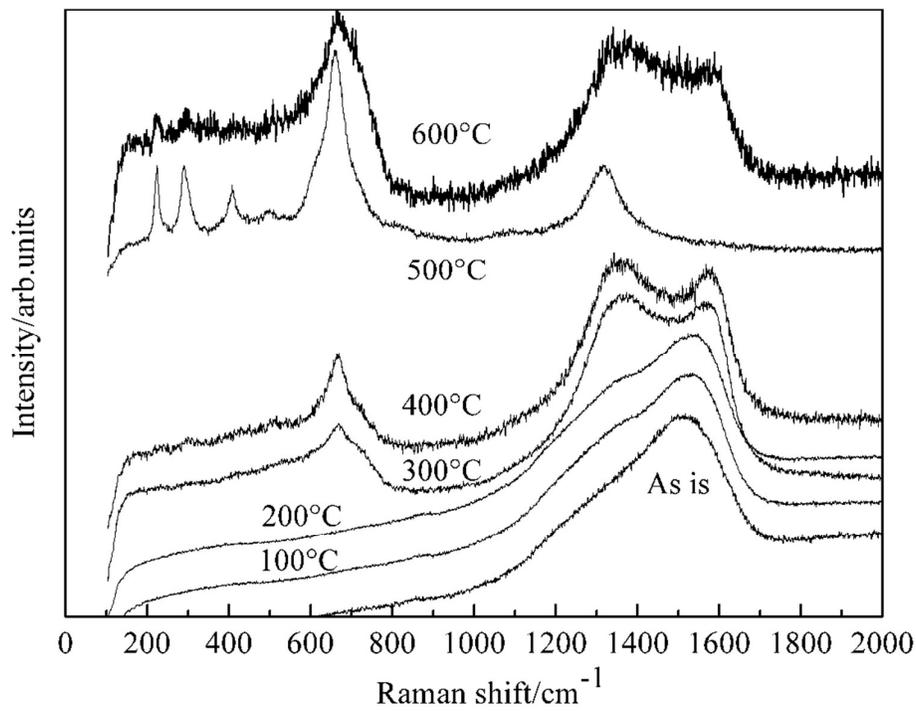


(g) 600 °C

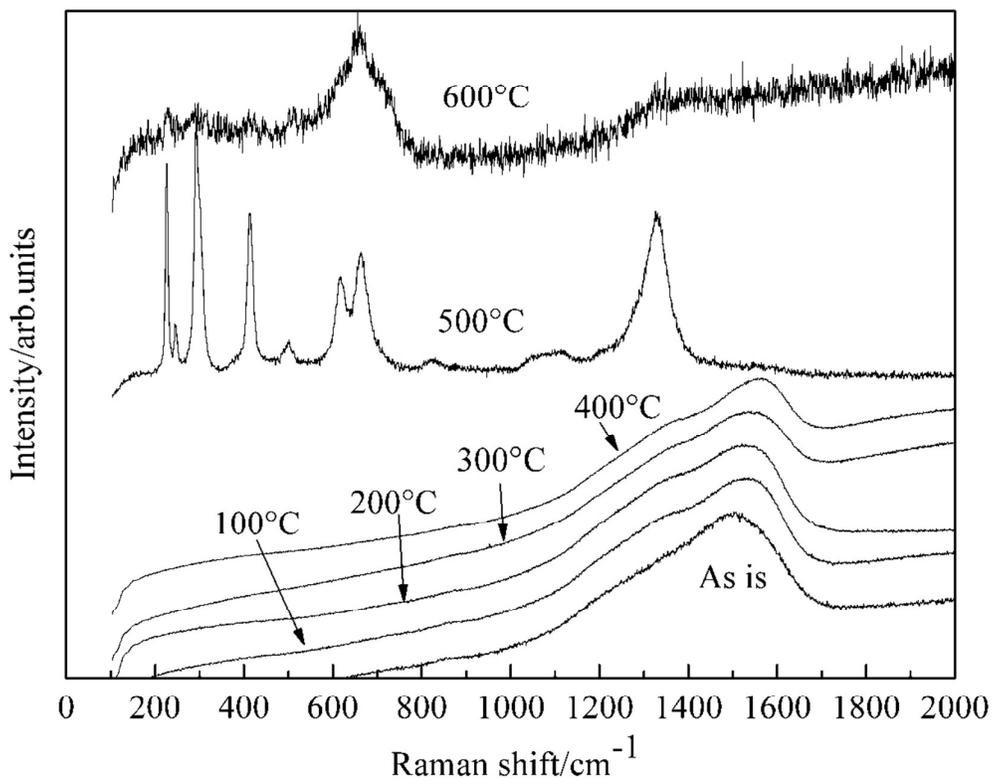
**Fig. 4** Surface topography of the worn surface on the flat under different temperatures



**Fig. 5** Surface topography of the worn surface on the flat under different temperatures

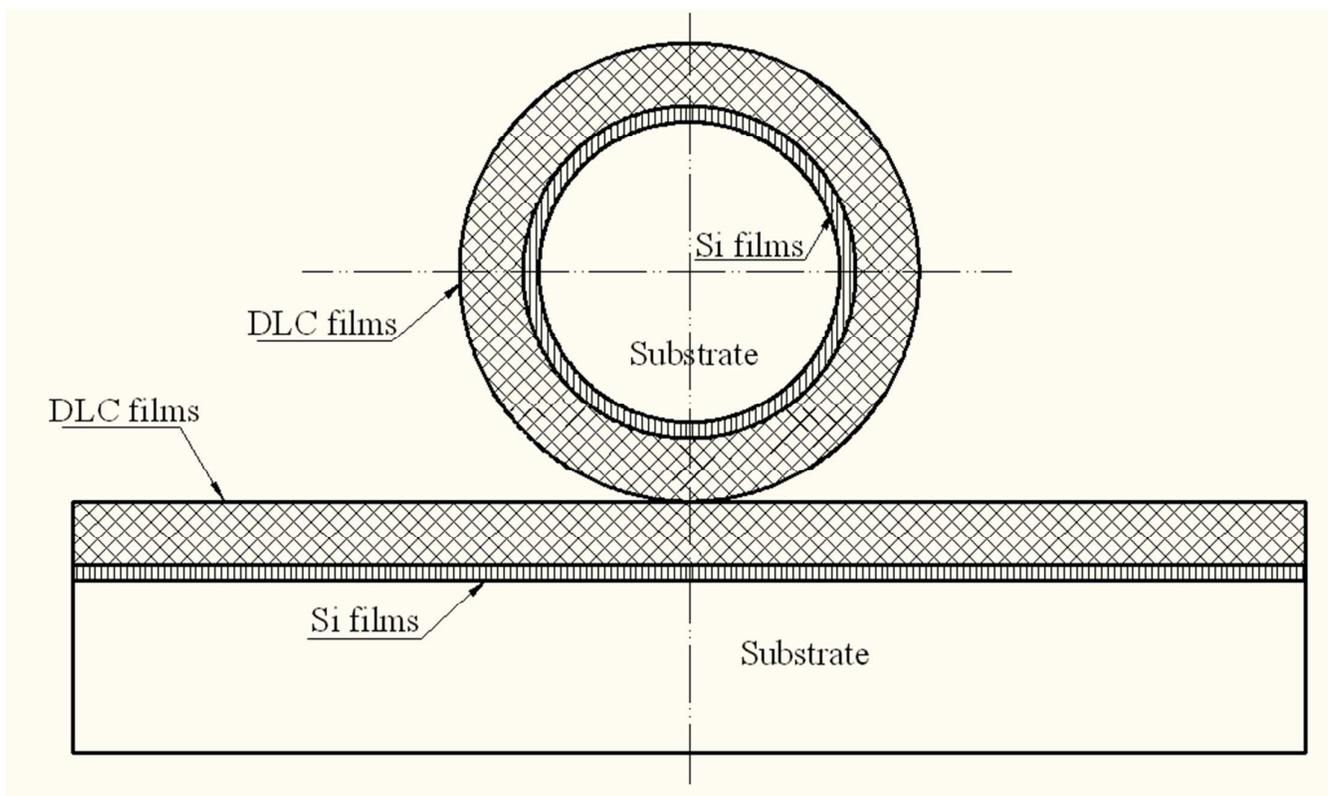


(a) Ball



(b) Flat

**Fig. 6** Raman spectroscopy of the worn surface on the friction pair under different temperatures



**Fig. 7** The schematic diagram of the friction pair

**Table 1** COF of the friction pair at initial stage under different temperatures

Temperature	25°C	100°C	200°C	300°C	400°C	500°C	600°C
COF	0.164	0.117	0.048	0.017	0.789	0.352	0.420

**Table 2** Average COF of the friction pair under different temperatures

Temperature	25°C	100°C	200°C	300°C	400°C	500°C	600°C
Average COF	0.127	0.067	0.018	0.376	0.228	0.539	0.008