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The Run-in Process for Stable Friction Fade-Out and Tribofilm Analyses by SEM and Nano-Indenter

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Manuscript received 22 June 2017; accepted 25 November 2017; published 31 December 2017

Abstract

It was shown in previous reports by authors that friction coefficients of the level of 0.0001 were achieved when ZrO₂ (Y-PSZ: yttria partially stabilized zirconia) pins were slid against diamond-like carbon (DLC) films in H₂-gas environment under heavy applied load of 63.7 N (friction fade-out, FFO). It was also shown that FFO continued long when the main H₂-gas flow was mixed with a small amount of aqueous-alcohol vapor. A tribofilm was formed at the contact area of ZrO₂ surface, and it was considered that the aqueous-alcohol vapor made the tribofilm strong. In the present research, the run-in process for achieving more stable FFO is investigated by varying the run-in pattern consisting of load step-up and aqueous-alcohol vapor addition, and the stable FFO continuing several hours is realized reproducibly. Then, before and after the FFO onset, the contact area on ZrO₂ surface is observed by SEM, and nano-indentation hardness of tribofilm is measured. It will be shown that a substance made of hydrocarbons with low melting temperature, low electrical conductivity and low nano-indentation hardness such as hydrocarbon polymers is formed on the tribofilm, suggesting the evolution of hydrocarbon gas at the sliding surface.

Keywords

DLC, run-in, zirconia, H₂ gas environment, catalytic reaction, friction fade-out, tribofilm, contact stiffness

1 Introduction

Tribological characteristics of diamond-like carbon (DLC) have been widely studied for various applications, because DLC generally exhibits low friction, high wear resistance, high hardness and chemical inertness [1]. Many reports have focused on the ultra-low friction characteristics of DLC with large hydrogen contents or have tested DLC in hydrogen environments [2-8]. In addition, recent studies have demonstrated that the effect of tribochemistry on the lubricity of DLC films in a hydrogen environment is significant [9] and that the formation of tribofilms via chemical reactions is particularly important for achieving superlubricity [10-13]. The term ‘superlubricity’ was originally proposed and defined by Hirano and Shinjo in 1990 [14] to describe a theoretical sliding state in which friction or resistance to sliding nearly vanishes. Hirano further suggested in 2014 [15] that the superlubricity occurs only at the frictional contact between two crystals. However, since the publication of Superlubricity [16] by Martin and Erdemir in 2007, in which superlubricity was defined as having a friction coefficient smaller than 0.01, many DLC researchers, including those mentioned

above, have adopted Martin’s definition for developments in carbon films in which a friction coefficient smaller than 0.01 is frequently attained [8,17-19].

We previously reported that DLC films with large hydrogen content showed significantly low friction coefficient when slid by ZrO₂ pins in H₂ gas environment [20]. We termed this behavior as friction fade-out (FFO) because the measured friction was close to a tribometer noise level of as low as 1.0 mN under an applied load of 4.9 N. This value corresponds to a friction coefficient of 0.0002, which is considerably smaller than the value for the superlubricity defined by Martin et al. [16] mentioned above. It was also shown FFO has load dependency, i.e. FFO was observed when an applied load was increased to, e.g. 30.4 N, which was considered advantageous for industrial applications. However, we encountered a problem, i.e. the friction coefficient frequently varied between 0.0001 and 0.01 even though the sliding and environmental conditions were not changed. We conducted many experiments and found that FFO stability could be achieved by adding an aqueous-ethanol vapor to main H₂ gas during the run-in stage [21].

More experiments were conducted for more stable FFO

by varying the run-in pattern consisting of load step-up and ethanol vapor addition to main H_2 gas flow. We consider the stable FFO can be achieved by a formation of a strong tribofilm on ZrO_2 surface during run-in process. It will be shown that a long-time FFO can be realized by the run-in pattern such that (1) the flow rate of main dry- H_2 gas is kept constant throughout the experiment, (2) an applied load is stepped up from 9.8 N to the maximum load, and (3) an addition rate of the aqueous-ethanol-vapored H_2 gas to main H_2 flow is kept constant during the load step-up but decreased gradually after finishing the load step-up. This run-in pattern ensures the reproducibility of stable FFO onset.

The tribofilm formed on ZrO_2 surface is considered to play an important role for stable FFO onset as mentioned above, the tribofilm was investigated carefully using an optical microscope, scanning electron microscopy (SEM), surface profilometry, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and time-of-flight secondary-ion mass spectrometry (TOF-SIMS) [20,21], in which we reported that the catalytic reaction of ZrO_2 is considered important for the onset of FFO. This involves the generation of gaseous substances that may have a gas lubrication effect together with the generation of highly H-passivated surfaces on DLC and ZrO_2 ; this significantly reduces the adhesive force. In the present study, SEM observations and nano-indentation tests are conducted to constrain the tribofilm characteristics at several stages of the FFO process, i.e. before and after the FFO onset. We will show that a type of hydrocarbon polymers are formed on the tribofilm surface during the progression of sliding tests involving FFO, and the formed polymers exhibit low electrical conductivity, low melting temperature and low indentation hardness.

2 Experiments

2.1 Test samples

An ion vapor deposition system was used in the present study to produce DLC films (NPS-330S, Nanotec Corp.) [20,21]. The source gas was introduced into the vacuum chamber and then ionized by thermal electrons emitted from an anode. Carbon or hydrocarbon ions were attracted by the pulsed negative-bias voltage applied to the electrode, on which sample substrates were fixed and ions were deposited onto the substrates. Si (100) wafers (R_a : 0.12 nm, thickness: 525 μ m) were prepared for use as sample substrates and were ultrasonically cleaned in ethanol, followed by acetone. After placing the Si substrate on the bias electrode in the chamber, the chamber was pumped down to a base pressure of 3.0×10^{-3} Pa and Ar^+ ion bombardment was performed for 30 min. For test samples, a 1200-nm-thick DLC layer was deposited using a $C_2H_6-H_2$ gas mixture with a bias voltage of -4.0 kV. The temperature of the heater near the sample was maintained at 230°C throughout the deposition.

H content of sample DLC was measured by Elastic Recoil Detection Analyzer (ERDA, KOBELCO, HRBS-1000). H content took larger value, e.g. 60%, at the surface due to several contaminants including H atoms, but decreased down to 20% by Ar^+ ion etching at the depth of 10 nm and kept constant at deeper layer [22,23]. As for C- sp^2 and C- sp^3 contents in DLC sample, the sample was also etched by Ar^+ ion, and raw data of XPS (XPS PHI Quantera SXM, Ulvac Phi and Inc.) spectrum was corrected by assuming the electron binding energy of $Ar2p$ to be 241.9 eV, then C1s peak was detected and deconvoluted into dominant C- sp^2 and C- sp^3 peaks and other small peaks

of C- sp , COH, CO, OCO and CN. The $sp^3/(sp^2 + sp^3)$ ratio was evaluated in this way to be 41% after 60 s of Ar^+ ion etched DLC, corresponding to a depth of 13 nm from the surface. So, we consider the original H content and $sp^3/(sp^2 + sp^3)$ ratio were 20% and 41%, respectively, of our sample DLC. The H content of 20% gives the density of DLC sample to be 2.0 gr/cm³ by assuming the sample was made only of H and C atoms. For more detail about the XPS evaluation, we employed a voltage of 284.6 eV and 285.4 eV for the C- sp^2 and C- sp^3 peaks as their binding energies, respectively. Then, we employed the Shirley method for baseline correction and the hybridized function of the Gauss function (80%) and the Lorentz function (20%) for the fitting curve [24,25]. Since the analysis by XPS is still said to be quantitatively questionable [26,27] due to the small difference between C- sp^2 and C- sp^3 peaks, we used the ratio $sp^3/(sp^2 + sp^3)$ only for a comparison among results obtained at subsequent measurements under the same conditions.

For the friction pins, ZrO_2 (Y-PSZ: yttria partially stabilized zirconia) balls with a 3/16-inch (4.76 mm)-diameter were used. The Young's modulus, Poisson's ratio and roughness R_a were 210.0 GPa, 0.31 and 6.1 nm, respectively. Assuming Hertzian contact between the ZrO_2 ball and the Si plate (Young's modulus: 130 GPa, Poisson's ratio: 0.28) under a load 63.7 N, a radius of contact of 109 μ m and a maximum contact pressure of 2.6 GPa were obtained.

2.2 Friction test procedure

Friction tests are conducted using a pin-on-disk tribometer (FPR-2000, RHESCA INC.) in the reciprocating mode. A ZrO_2 pin is placed on a DLC sample fixed on the disk. The disk reciprocates at a constant speed of 7.2 mm/s, with a single sliding distance of 4.3 mm. The test area including the disk and pin is covered with a double plastic casing without a seal. Thus, experiments are conducted under atmospheric pressure. In the present tribometer, the DLC sample is fixed on a gimbal-mounted moving disk and the dead weight is applied directly onto the ZrO_2 pin which slides on the sample.

As for the low friction measurement, Schmitz [28] showed that the misalignments of the load and friction force from the normal and tangential directions, respectively, leads an error in the calculation of friction coefficient, particularly the latter misalignment has a huge effect when the friction force is small. The misalignment of a friction-measurement sensor is frequently brought about by loading itself. In the present tribometer, in order to avoid these misalignments, the DLC sample is fixed on a gimbal-mounted rotating disk and the dead weight is applied directly onto the ZrO_2 pin which slides on the sample. The pin is supported by a counter-balanced and rigid swing-bar. The torque exerted to the bar is measured by a load cell, and the bar and load cell are connected by a thin rod with pin-joints at both ends. Thus, the friction force measurement is hardly affected by loading, and the possible error in the friction measurement in our system is only a thermal drift of the equipment, which is smaller than 1 mN [21] and corresponds to friction coefficients of approximately 1.6×10^{-5} for a load of 63.7 N. In addition, zero point of friction is checked before and after every measurement. Figure 1 shows an illustration of the testing system used for the test conducted in H_2 gas environment.

3 Results and discussions

3.1 Improvement in run-in pattern

It was found through many experiments [20,21] that the

Fig. 1 Schematic diagram of gas supply and friction tester

Fig. 2 Schematic diagram of test process

stable FFO can be achieved by the run-in process comprising (1) main dry H_2 gas supply to the test area throughout the friction test, (2) an applied load step-up from low load to the maximum load, and (3) a small amount of aqueous-ethanol-vapored H_2 gas is added to the main H_2 gas. To improve the run-in process, we varied the supply rate of main H_2 gas, timing and rate of decrease of aqueous-ethanol-vapored H_2 gas addition, height and width of load step-up, and the maximum load. We finally obtained the run-in pattern, which ensures reproducibility of stable FFO, as shown in Fig. 2, i.e., (1) the flow rate of main dry- H_2 gas, Q_{H_2} , is kept constant throughout the experiment, (2) an applied load, W , is stepped up from 9.8 N to the maximum load, W_{max} , which is usually larger than 40 N, and (3) the addition rate of the aqueous-ethanol-vapored H_2 gas, q_{et} , to main H_2 flow is kept constant during the load step-up but decreased gradually after finishing the load step-up.

3.2 FFO under improved run-in pattern

Figure 3 shows an example of FFO obtained under the improved run-in pattern mentioned in 3.1 section. We adopt $Q_{H_2} = 4.3$ slm (standard liter per minute), $W_{max} = 63.7$ N, and q_{et} (initial) = 180 sccm (standard cubic-centimeter per minute), and q_{et} (final) = 2 sccm in this experiment. FFO appears when supply rate of aqueous-ethanol-vapored H_2 gas is 4 sccm denoted by "a" in figure and continued about four hours. Another example of FFO is shown in Fig. 4 that the friction coefficient decreases to about 0.0001 when aqueous-ethanol-vapored H_2 -gas supply is 6 sccm denoted by "b" in figure, then interestingly further decrease in friction coefficient is observed when aqueous-ethanol-vapored H_2 -gas supply is 4 sccm which is denoted by "c"

Fig. 3 Friction coefficient trace

Fig. 4 Friction coefficient trace

Fig. 5 Friction coefficient v.s. Relative humidity

in figure, suggesting that the relative humidity, %RH affects the friction coefficient. Thus, a hygrosensor is fixed inside the inner case of friction tester, and the relative humidity at the test area is measured. Figure 5 shows the change in friction coefficient against relative humidity of four experiments including those of Figs. 3 and 4. It is seen from the figure that the friction coefficient decreases monotonically with the relative humidity,

and FFO occurs when %RH becomes 1% or smaller in all cases.

We consider from these experiments that the load step-up is the process of tribofilm formation [29] on ZrO_2 surface from hydrocarbons transferred from DLC and ethanol as raw materials. Water vapor contributes to the tribofilm formation in a way of substances like adhesives, since stable FFO does not occur when dehydrated ethanol is used instead of aqueous-ethanol. After forming a proper tribofilm, however, water molecules are considered to interfere the onset of FFO, and the decrease in an addition of aqueous-ethanol-vapored H_2 gas triggers FFO onset.

3.3 SEM observation of tribofilm before and after FFO

We investigated the mechanism of FFO in our previous papers [20,21] on the basis of observations and measurements made using an optical microscope, SEM, a surface profile meter, XPS, Raman spectroscopy and TOF-SIMS, and found that the tribofilm formed on the ZrO_2 surface was thin and showed weak adhesion; which caused blisters on the film. It was also found that short-chain hydrocarbons were predominant both in the tribofilm [21] and in the wear track on the DLC samples [20] after FFO terminated.

To evaluate the difference in the tribofilm on ZrO_2 before and after FFO onset, we conducted three separate experiments under the same run-in pattern with the same parameter values. They are $Q_{\text{H}_2} = 4.3 \text{ slm}$, $W_{\text{max}} = 63.7 \text{ N}$, and q_{et} (initial) = 180 sccm. The first and second experiments were stopped during load step-up at 20 N and after the load step-up at 63.7 N, respectively, and the third one was stopped about 16 minutes after the onset of stable FFO, which occurred when $q_{\text{et}} = 40 \text{ sccm}$ as shown in the figure. "A", "B" and "C" in Fig. 6 denote these three timings, in other words, three experiments were stopped at A, B and C, and three samples of ZrO_2 pins were prepared, which we refer as sample A, B and C, respectively. It is noted that three friction traces were almost overlapped, thus, only the third experiment is shown in Fig. 6. We observed tribofilm surface using SEM (Elionix Inc. ERA-9000), by which the secondary ion images were mainly taken at a very low accelerating voltage of 1.0 kV since the tribofilm was found to be sensitive to electron irradiation.

Figure 7 shows SEM observations of the tribofilm of sample A. It is seen from Fig. 7(a) that the tribofilm has already formed at the contact area, and contains irregularities at the center of the tribofilm, as shown in Fig. 7(b). The tribofilm possibly detaches from the ZrO_2 surface and forms surface irregularities. It can also be seen that the tribofilm is peeled off in the peripheral region, as shown in Fig. 7(c); this is attributed to the higher coefficient of friction of about 0.03, as shown in Fig. 6.

Fig. 6 Timings of SEM observation and nano-indentation

Fig. 7 SEM observation at tribofilm of sample A
(a) Overall tribofilm, (b) center of tribofilm
and (c) peripheral region of tribofilm

Figure 8 shows SEM observations of the tribofilm of sample B. This sample was prepared after the load step-up to 63.7 N at the friction test. It is interesting that the friction coefficient decreases by half as the load is stepped-up three times from sample A to B, as shown in Fig. 6. Figures 8(a) and (b) show the overall and the center of tribofilm, respectively. It is seen from Fig. 8(b) that the tribofilm contains irregularities at the center, but the shape of these irregularities is different from those shown in Fig. 7(b). The irregularities in Fig. 8(b) are narrow and are aligned in the transverse direction to sliding. Note that the sliding marks are visible in Fig. 8(a), and the sample was not rotated during SEM observations. The change in the shape of the irregularities is caused during the load step-up and suggests the detachment of tribofilm from ZrO_2 surface. Figure 8(a) shows that "white" substances are formed on the tribofilm, which were not seen in Fig. 7. Magnified images of these "white" substances are shown in Fig. 8(c), in which they appear in white sharply without being fogged by halation. It should be noted that the "white" substances disappear and are indistinguishable from the background in a backscattered electron imaging mode at SEM observation. These observations indicate that the "white" substances are the same atomic composition as the background materials but exhibit lower electrical conductivity compared to the background. Since hydrocarbons are predominant at the tribofilm [21], we conclude that the "white" substances are C-sp³ rich compared to the background materials.

Figure 9 shows SEM observations of the tribofilm of sample C. It is seen from Fig. 9(a) that many "white" substances are

Fig. 8 SEM observation at tribofilm of sample B
(a) Overall tribofilm, (b) center of tribofilm
and (c) white substance formed on tribofilm

present on the tribofilm. The magnified image of one of these “white” substances is shown in Fig. 9(b), and magnified further in Fig. 9(c). These figures show that many holes exist on the surface. Fig. 9(c) corresponds to the dotted square in Fig. 9(b) and is taken 34 seconds after Fig. 9(b). Comparing Fig. 9(c) with the dotted area in Fig. 9(b), it is observed that the holes are enlarged and some holes have become interconnected. These changes occur during SEM observations despite the very small accelerating voltage of 1.0 kV. This suggests that the “white” substances have low melting temperature as one of thermal characteristics.

3.4 Nano-indentation test before and after FFO

To obtain more information of the mechanical properties of tribofilm, nano-indentation tests are conducted. Since the tribofilm looks inhomogeneous from overall appearance, conventional nano-indentation tests are conducted at several parts of the tribofilms of the same samples investigated by SEM in previous section. We use a high performance nano-indentation equipment (Elionix Inc. ENT3100) having a resolution of 0.3 nm of indenter displacement and an applied load ranged from 0.5 μ N to 10 mN. Tip effect calibration tests are conducted at the beginning of tests using fused silica and ensured accuracy, and the loading and unloading curves are checked for all tests. An indentation load is set to be 100 μ N for all measurements, resulting in an indentation depth in the range of 10 nm to a maximum of 45 nm.

Thirty points at the tribofilm on sample B are tested, which

Fig. 9 SEM observation at tribofilm of sample C
(a) Overall tribofilm, (b) “white” substance
formed on tribofilm and (c) “white” substance
in magnified scale corresponding to the dotted
square area in (b). (c) was taken 34 sec after (b)

Fig. 10 Nanoindentation measurement points on tribofilm of sample B

are lapped over SEM image of Fig. 8(a) and marked in Fig. 10. Figure 11 shows an example of load-unloading curves of points 1 to 10 marked in Fig. 10 obtained by nanoindentation tests for sample B. It is seen from Fig. 11 that the indentation depth distributes widely from 14 nm (at point 10) to 28 nm (at point 1), which reflects the wide distribution of nanoindentation hardness from 5 GPa (at point 1) to 26 GPa (at point 10) as shown in Fig. 12. In Fig. 12, the results of nano-indentation

Fig. 11 Loading and unloading curves at nano-indentation tests at the center of tribofilm. Point numbers correspond to those marked in Fig. 10

Fig. 12 Contact stiffness against nanoindentation hardness for tribofilm of sample B

hardness are shown against contact stiffness. Regarding the contact stiffness, Oliver and Pharr [30] reported loading and unloading curves in terms of material elasticity and plasticity characteristics. During loading, deformation is assumed to be both elastic and plastic in nature, whereas, during unloading, it is assumed that only the elastic displacements are recovered. They also mentioned that finite element simulations have shown that reversible plastic deformation is usually negligible [31]. Thus, the unloading curve almost reflects the pure elastic characteristics of a sample, and the contact stiffness, S , is defined as the slope of the upper portion of the unloading curve:

$$S = \frac{dP}{dh} \quad (1)$$

where P and h are the applied load and the displacement relative to the initial undeformed surface, respectively.

It is seen from Fig. 12 that the measured hardness distributes widely on the tribofilm. The tribofilm is relatively hard at peripheral 1 where the tribofilm looks smooth by SEM measurement, on the other hand, the tribofilm is very soft at peripheral 2. These measurements suggest that the peripheral 1 is made of transferred DLC materials and compressed hardly by pressure, while peripheral 2 seems to be made of accumulated wear debris. On the other hand, the hardness at the center of tribofilm varies widely from 5 GPa to 18 GPa.

Thus, we conducted more nano-indentation tests at the center of tribofilm using samples A and C, and the results are compared with sample B, as shown in Fig. 13. It is seen from the figure that the indentation hardness decreases with sliding

Fig. 13 Nano-indentation hardness of samples A, B, and C

Fig. 14 Contact stiffness of samples A, B, and C

numbers, and considerably decreases in sample C, i.e. after FFO onset. On the other hand, the contact stiffness shown in Fig. 14, S , derived by the slope of unloading curve, does not change so much among the tests A, B and C, and they are like that of ZrO_2 . Bars in Figs. 13 and 14 denote the standard deviation of the measured data.

We can make more profound discussion in view of the fact that nanoindentation hardness, H_i , comprises surface elasticity and plasticity, on the other hand, contact stiffness, S , reflects only surface elasticity. Wider variation of H_i comparing to smaller variation of S , as shown in Fig. 12, indicates that the plasticity of tribofilm distributes widely over the tribofilm. It is also seen from Fig. 12 that the contact stiffness takes similar value to that of ZrO_2 , indicating that the surface stiffness is almost covered by that of ZrO_2 and the tribofilm itself is very plastic. From these considerations, we can see from Figs. 13 and 14 that the surface brittleness of tribofilm increases with sliding numbers (Fig. 13), but that the elasticity of ZrO_2 does not change with sliding numbers (Fig. 14).

The result that H_i decreases with sliding numbers supports the claim made in the discussion of SEM observations in the previous section that the substances formed on the tribofilms by FFO are likely hydrocarbon polymers. The process that produces these substances is closely related to the mechanism of FFO, such that the hydrocarbon gas may be evolved from the contact surface including tribofilm and supplied ethanol by the catalytic action of ZrO_2 , then polymerized on the tribofilm by extensively high contact pressure. The possibility of evolved-gas-induced super-low friction will be discussed elsewhere [32].

4 Conclusions

A stable Friction fade-out (FFO) is achieved by improving the run-in pattern, such that (1) the flow rate of main dry- H_2 gas is kept constant throughout the experiment, (2) an applied load is stepped up from 9.8 N to the maximum load, and (3)

an addition rate of the aqueous-ethanol-vapored H_2 gas to main dry- H_2 gas is kept constant during the load step-up but decreased gradually after finishing the load step-up. It is shown that the improved run-in pattern ensures the reproducibility of the onset of stable FFO. Tribofilms formed on ZrO_2 pins were observed by SEM and investigated by nano-indenter before and after FFO onset. It is shown that "white" substances are formed on the tribofilm observed by secondary ion imaging mode. It is shown these substances are made of hydrocarbons and exhibit low melting temperature, low electrical conductivity, and low nano-indentation hardness. It is also shown by nano-indentation test that the tribofilm is very brittle, and the brittleness increases with sliding. It is discussed that these "white" substances may be formed on the tribofilm by the polymerization of hydrocarbon gas evolved from the contact surface under heavy applied pressure.

Acknowledgements

The authors are grateful to Elionix INC. for providing the measurement facilities, and especially to Ms. Y. Omata and Mr. T. Ito, Elionix INC., for their suggestions on the measured results.

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