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Effect of pH on the liquid superlubricity between Si_3N_4 and Glass achieved with phosphoric acid

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Abstract

In the present study, the pH dependence of liquid superlubricity between Si_3N_4 and glass achieved with phosphoric acid solution was investigated. It shows that the superlubricity can be achieved only when the pH value is in the range of 0.75-2. To reveal the mechanism, the evolutions of confined solutions with different pH values between two friction surfaces were investigated by the online observation. It is seen that the superlubricity appears when the confined solution between two friction surfaces forms the starvation state. When pH is in the range of 0.75-1.75, the starvation state can be formed as long as the running-in period is end. When pH is in the range of 1.75-2, the starvation state can be formed by adding the amount of phosphoric acid molecules in the contact region, leading to the transformation from unstable friction state to superlubricity. When pH is in the range of 0-0.75, the superlubricity cannot be obtained no matter how to change test conditions, because of high contact pressure and having no time for tribochemical reaction between friction surfaces and hydrogen ions. When pH is greater than 2, the friction keeps high value because there are not enough hydrogen ions adsorbed on the friction surfaces to make them positively charged.

Keywords

Superlubricity, tribochemistry, aqueous lubrication, friction surface

Introduction

The concept of superlubricity, proposed by Hirano and Shinjo in 1900s, is used to describe the physical phenomenon that the friction force between two surfaces vanishes completely.[1, 2] But in actual experimental condition, when the ratio of friction force to applied load is less than 0.01 ($\mu<0.01$), it is called as superlubricity.[3] Because the superlubricity can reduce energy dissipation in mechanical system effectively, the investigations on superlubricity are becoming a hot research in recent years.[4-7] At present, there are several solid lubricants found having superlubricity property, such as DLC,[8, 9] MoS_2,[10] and graphite.[11] In addition to this, some liquid lubricants also have superlubricity property, for example, polymer brushes with water,[12, 13] ceramic materials with water,[14, 15] glycerol solution with acid or polyhydric alcohol,[16-18] and some kinds of polysaccharide mucilage from plants.[19, 20] Although all of them can realize an ultralow friction coefficient less than 0.01, the superlubricity mechanism of them is totally different. For solid lubricant, the superlubricity is usually attributed to incommensurate surface lattice structures or weak dispersive interlayer interaction or coulomb repulsion at the contact.[21-23] For liquid lubricant, there are at least three lubrication models, such as tribochemistry reaction between ceramic and water, forming hydrogen bond network with water molecules, and forming hydration layer.[14, 18, 24] Therefore, to find out more kinds of superlubricity materials and establish a new superlubricity theory is the most important task for superlubricity researchers.

Recently, the liquid superlubricity with the lubrication of phosphoric acid solution was obtained by our group.[25] It is found that the achievement of superlubricity is closely related to the hydrogen ions and the hydrogen bond network between phosphoric acid and water molecules.[26, 27] However, there is still a problem needing to solve; that is the relationship between hydrogen ions and superlubricity (we found that the superlubricity is closely dependent on the pH value of phosphoric acid solution). If this problem is solved, it would not only give a better comprehension on the superlubricity mechanism of phosphoric acid, but can also instruct us to design new liquid superlubricity materials. Therefore, in the present work, the relationship between friction behavior and pH value of phosphoric acid was investigated and the mechanism of influence of pH value on superlubricity was discussed according to the online observation.

Materials and method

The phosphoric acid (H_3PO_4) in the test is a commercial product (Beijing Chemical works) with a mass fraction of 85%. Before test, it was diluted by deionized water to different pH values (pH=0, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, and 2.5, measured by a standard pH meter). The friction pairs are a Si_3N_4 ball with a diameter of 4 mm (obtained from Shanghai Research Institute of Materials) and a glass slide with the surface roughness (Ra) of about 5 nm (part of the common glass slide for microscopy). Both the ball and the glass were cleaned in an ultrasonic bath with acetone and ethanol each for 15 min sequentially, and then they were washed by deionized water and dried by compressed air.

The friction coefficient was measured on a Universal Micro-Tribotester (UMT-3, Bruker, USA) with a rotating mode of ball-on-disk (Fig. 1). Before test, the H_3PO_4 solution was introduced between the ball and the disk by dropping a few droplets (10 μL). The applied load on the disk was 3N, corresponding to a maximal contact pressure of 700 MPa. The rotation speed of the disk was 180 rpm and the radius of the sliding track on the disk was 3 mm, corresponding to a linear sliding speed of 0.056 m/s. The ambient temperature was about 25 ℃ and the relative humidity was about 25%. To ensure the measuring accuracy of friction coefficient, the measurement errors in the test were also eliminated by the method in Ref 26.[28]

The apparatus for observing the confined solution between two friction surfaces online was shown schematically in Fig. 1 (the radius of the sliding track on the disk is the same as that in UMT-3). An optical microscope (×20) was located above the contact region between the two friction surfaces. The white light from a halogen lamp was shone through the microscope on to the contact region, and the views of the contact region were captured by using a digital CCD camera at the same location on the same scale. Although the friction force cannot be measured by the in situ observation apparatus, the test conditions (speed, load and environment) and friction pairs and lubricant in the online observation were all the same as those in the friction tests to ensure that the evolution of friction coefficient with time is in accordance with the evolution of contact region with time.

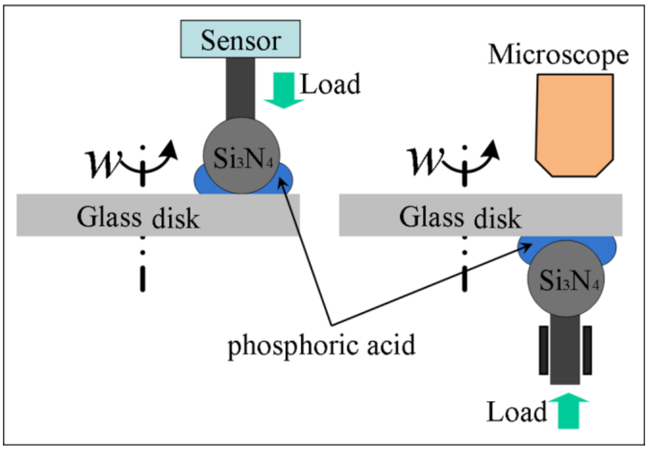

Fig. 1 Schematic illustration of the apparatus for measuring friction coefficient and observing confined solution in the contact region online.

Results and discussion

Figure 2 shows the evolutions of friction coefficient with time under the lubrication of H_3PO_4 solution with different pH values. It is found that when the pH value of H_3PO_4 solution is 0 and 0.5, the friction coefficients can reduce to 0.021 and 0.012 respectively after a running-in period and then have no further reduction. It indicates that the superlubricity cannot be obtained in the two cases. However, when the pH value of H_3PO_4 solution becomes 1 and 1.5, the friction coefficients can reduce to less than 0.01 after a running-in period of 320 s and 600 s respectively, which enters the superlubricity regime. When the pH value of H_3PO_4 solution increases to 2, the friction coefficient can reduce to 0.011 after a running-in period of 600 s, but it has a sudden rise from 0.011 to 0.5 at the end of the test. When the pH value of H_3PO_4 solution increases further to a higher value (pH=2.5), the evolution of friction coefficient with time is totally different from that for pH<2. It is seen that the friction coefficient cannot reduce anymore. Instead it keeps a high value (greater than 0.5) all the time.

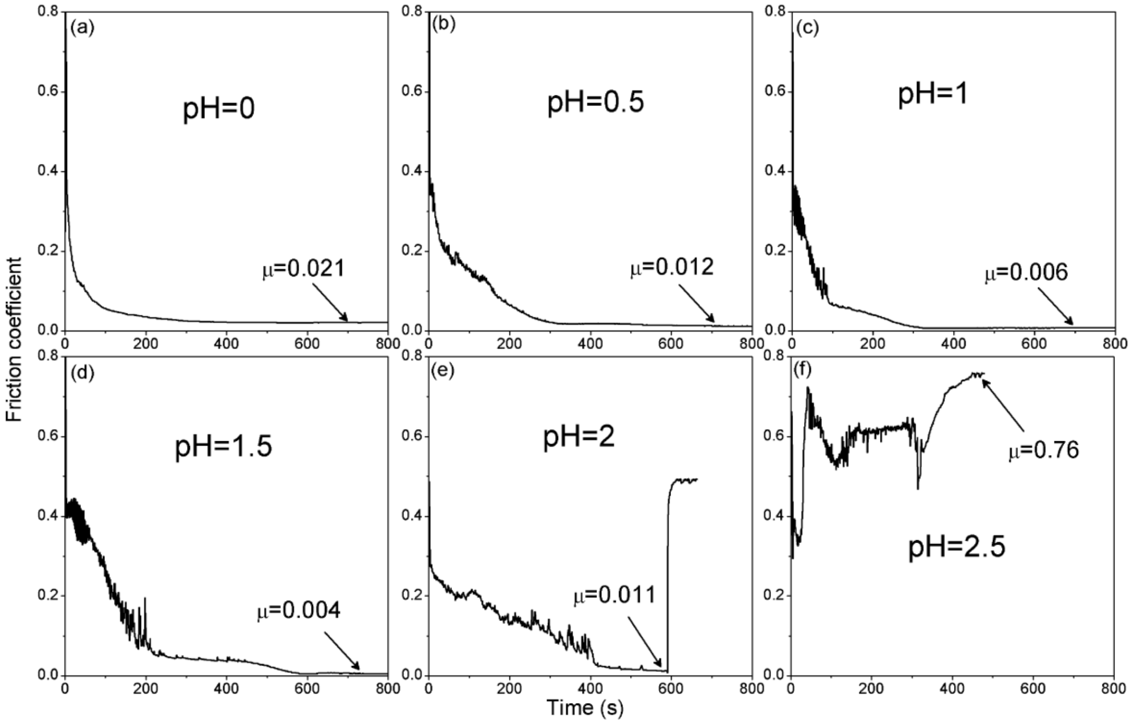

Fig. 2 Evolution of friction coefficient with time under the lubrication of H_3PO_4 solution with different pH values. (a) pH=0, (b) pH=0.5, (c) pH=1, (d) pH=1.5, (e) pH=2, and (f) pH=2.5.

According to the friction results above, it can be found that the pH value of H_3PO_4 solution has great effect on the final friction state. According to the further subdivision of pH value, the relationship between final friction state and pH is shown in Fig. 3. It can be seen that only when the pH is in the range of 0.75 to 1.75, can the superlubricity state ($\mu<0.01$) be achieved. When the pH is less than 0.75, the final friction coefficient is in the range of 0.01 to 0.05 (the low friction state). When the pH is in the range of 1.75 to 2.0, the friction coefficient can reduce to about 0.01-0.02, but it would increase to a high value at the end of test (the unstable friction state). When the pH is greater than 2, the friction coefficient keeps a high value ($\mu>0.1$) till the end of test (the high friction state).

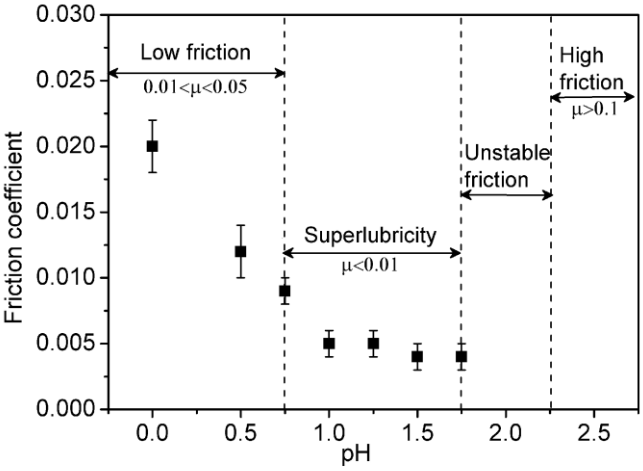

Fig. 3 Relationship between friction state and pH value of H_3PO_4. The friction coefficient for every pH value was measured in the same condition for five times. The statistical error is the standard deviations of these five values.

In our previous work, it is found that when the pH value of acid solution (such as sulphuric acid, lactic acid and oxalic acid) is less than 2, the friction coefficient can reduce to about 0.05 after a running-in period, which is attributed to the surface protonation reaction between hydrogen ions and friction surfaces ($SiOH+H^+ \rightarrow SiOH_2^+$, $SiO^-+2H^+ \rightarrow SiOH_2^+$) during the running-in process.[26] It can lead to the formation of many positively charge surface sites to produce the stern layer and the electrical double layer to lower friction force. As for H_3PO_4, it can be inferred that the mechanism of friction reduction is the same as the other acids when pH<2. When pH>2, the ionization of hydrogen ions from surfaces ($\equiv SiOH \rightarrow \equiv SiO^- + H^+$) would tend to dominate and thereby there are not enough amount of hydrogen ions to be adsorbed on the two friction surfaces to make the surfaces positively charged,[29] which is the reason why the friction keeps high value in the whole test. However, this lubrication model of surface protonation reaction above can only explain why the friction coefficient decreases in the running-in period. It cannot give an explanation why the superlubricity can only be obtained in the range of 0.75-1.75. To investigate this phenomenon, the evolution of contact region with test time between two friction surfaces was observed and analyzed by online apparatus.

First, the contact region between two friction surfaces lubricated by H_3PO_4 with a pH of 1.5 was investigated, as shown in Fig. 4. At the early stage of test (from 0 s to 100 s), there was no change with time in the contact region except for the wear region increasing. But when the test time lasted for 350 s, it is seen that the volume of solution confined between two surfaces began to reduce in the frame size of CCD camera due to the evaporation of free water in the solution. With test time increasing continuously, a bright “tail” appeared in the outlet region at the time of 450 s (Fig. 4 (d)). After that, the length of the “tail” became longer gradually with time. At last (525 s), it broke the edge of surrounding solution, and expanded to the whole track, as shown in Fig. 4 (e). At the same time, there was also a change appeared in the inlet region. It is found that a small bright meniscus was appeared in the inlet region (Fig. 4 (e)). And then it began to expand towards the contact region. At last, the confined solution between two surfaces presented “H” distribution, which is the same as the distribution of lubricant in the lubricating state of starvation.[30] Even if we tested it for a long period, the distribution of lubricant would keep constant due to the nonvolatility of phosphoric acid.

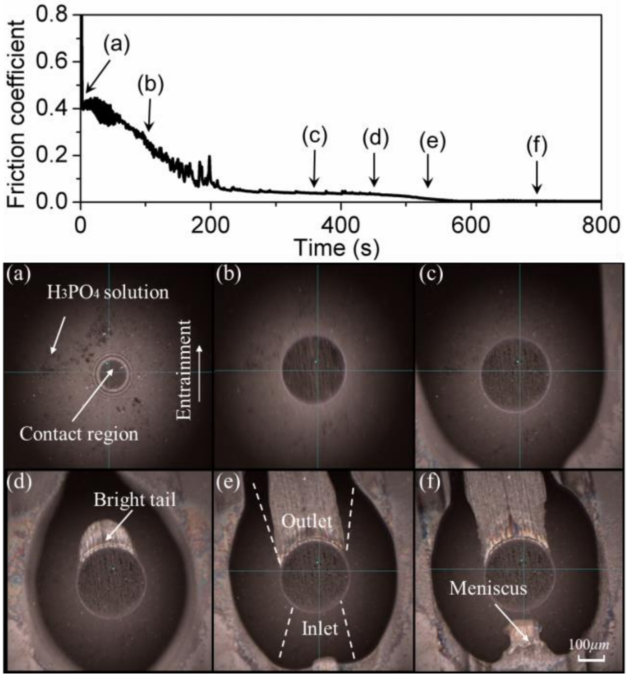

Fig. 4 Optical images of contact region between two surfaces lubricated by H_3PO_4 with a pH of 1.5. (a), (b), (c), (d), (e), and (f) correspond to the six moments on the friction coefficient curve. All of these images were caught at the same location on the same scale.

Second, the contact region between two friction surfaces lubricated by H_3PO_4 with a pH of 0 was investigated, as shown in Fig. 5. It is found that the wear region increased with time at the early stage (from 0 s to 100 s). At the time of 100 s (Fig. 5(c)), there appeared a small bright “tail” in the outlet region, and then the “tail” began to expand gradually with time. At the time of 400 s (Fig. 5(e)), the length of the “tail” reached the maximum (about 50 μm). After that, the shape of the “tail” kept constant, and the friction coefficient also kept constant. In addition, it is found that there was no change in the inlet region and the confined solution between two friction surfaces suffused the whole screen of CCD camera in the whole test, which is totally different from the final starvation state for pH=1.5.

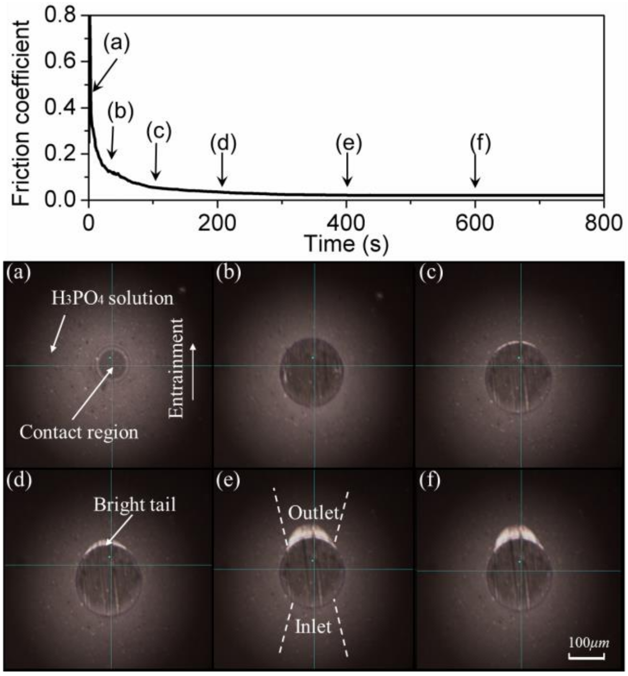

Fig. 5 Optical images of contact region between two surfaces lubricated by H_3PO_4 with a pH of 0. (a), (b), (c), (d), (e), and (f) correspond to the six moments on the friction coefficient curve. All of these images were caught at the same location on the same scale.

Third, the contact region between two friction surfaces lubricated by H_3PO_4 with a pH of 2 was investigated, as shown in Fig. 6. It is found that the wear region increased with time at the early stage (from 0 s to 300 s), which was the same as that for pH=1.5 and pH=0. After that, it can be seen that the volume of solution confined between two friction surfaces became less and less with time. When the friction coefficient reduced to 0.012 (t=550 s), there was almost no excess solution observed around the contact region (Fig. 6(e)). And after a short period (t=610 s), a severe wear was seen in the contact region and in the whole track (Fig. 6(f)), which indicates that there is no liquid film to separate the two friction surfaces apart (dry friction). At the moment, the friction coefficient rose to 0.5 suddenly.

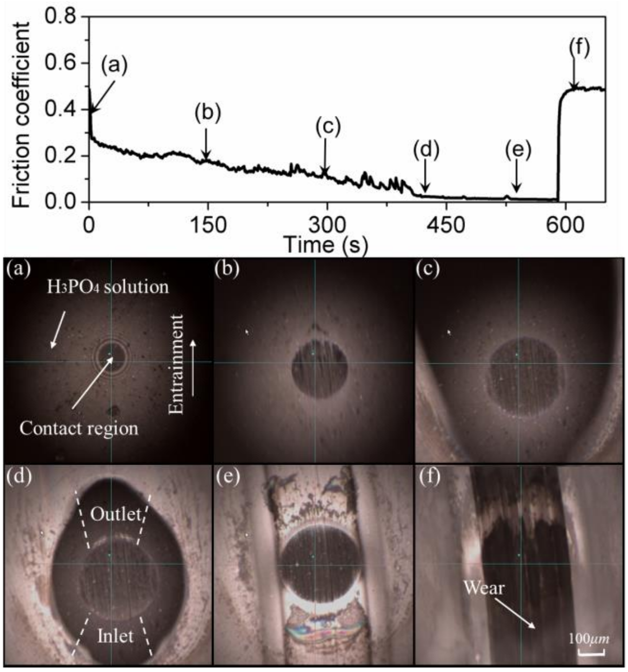

Fig. 6 Optical images of contact region between two surfaces lubricated by H_3PO_4 with a pH of 2. (a), (b), (c), (d), (e), and (f) correspond to the six moments on the friction coefficient curve. All of these images were caught at the same location on the same scale.

Comparing with the evolutions of contact region for the three different pH values, it is found that the evolutions of contact region with different pH values are the same at the early stage of test. But after that, different pH values correspond to different evolutions of contact region. When pH=1.5, the superlubricity can be achieved after a running-in period. From Fig. 4, it is seen that the solution confined between two friction surfaces presents "H" distribution (forming the starvation state) when superlubricity appears. At the moment, there is a thin film with a hydrogen bond network between H_3PO_4 and H_2O molecules adsorbed on the whole track.[20] When pH=0, the distribution of solution confined between two friction surfaces is different from that for pH=1.5. There is a bright "tail" in the outlet region but there is no bright meniscus in the inlet region, and moreover, the solution suffuses the whole screen of

CCD camera, corresponding to a friction coefficient of 0.021. When pH=2, there is no excess solution left in the contact region finally, leading to a very high friction. According to the relationship between friction coefficient and the distribution of solution, it can be inferred that the requirement for superlubricity is the solution confined between two surfaces forming the starvation state.

The starvation usually occurs in the cases of high speed, high viscosity and limited lubricant supply.[31] In these tests, the speed and the viscosity of lubricant (after the running-in period) are almost the same for the three different pH values. Therefore, they are not the reasons for the starvation. Thus, the only factor for starvation is the limited amount of solution available to the contact, leading to the solution fed in the inlet and outlet of the contact being deficient to provide a fully flooded condition. From Fig. 4(f), it can be seen that there remains a small volume of solution confined between two friction surfaces to form the starvation state when pH=1.5, which is in accordance with the factor for starvation above. As for pH=0 (Fig. 5(f)), it can be seen that the volume of solution confined between two friction surfaces is much larger than that for pH=1.5, which is the reason why the starvation state cannot be formed. As for pH=2, the result is just contrary, and it is found that there is no excess solution left between two friction surfaces to form the starvation state. Comparing with these results, it can be inferred that if we reduce the initial volume of solution added in the contact region when pH=0 or increase the initial volume of solution added in the contact region when pH=2, the final volume of solution confined between two surfaces would become limited amount (just like Fig. 4(f)) to form the starvation state and thereby the superlubricity is also possible to be achieved according to the requirement for superlubricity (forming the starvation state).

To further confirm this inference, we reduced the initial volume of solution from 10 μL to 0.5 μL when pH=0, and increased the initial volume of solution from 10 μL to 30 μL when pH=2. The friction coefficient results and the final lubrication state are shown in Fig. 7(a) and 7(b). It is found that when pH=0, the friction coefficient reduces to 0.02 after a short period of 35 s, and then it keeps constant. It suggests that the superlubricity cannot be achieved even if we reduce the initial volume of solution to a very small value to form the starvation state when pH=0. But when pH=2, after a long period of 500 s, the starvation state can be formed and the friction coefficient can reduce to 0.006, which indicates that the superlubricity can be achieved if the initial volume of solution increases to a higher value to form the starvation state when pH=2. According to this result, it can be inferred that the reason for the unstable friction state when pH=2 is that the initial volume of H_3PO_4 solution is too small. To further confirm this inference, we added some H_3PO_4 solution (20 μL) in the contact region immediately after testing H_3PO_4 solution (pH=2) for 550s (Fig. 6(e)). It can be found that the stable superlubricity state can be achieved after a running-in period. Therefore, it can be concluded that the stable superlubricity state can be achieved as long as there are enough amounts of H_3PO_4 molecules left in the contact region to form the starvation state when pH=2. However, as for pH=0, it can be confirmed that the initial volume of H_3PO_4 solution is too large to form the starvation state is not the only reason why the superlubricity cannot be achieved. In other words, there exist other factors that probably have influence on superlubricity state when pH=0.

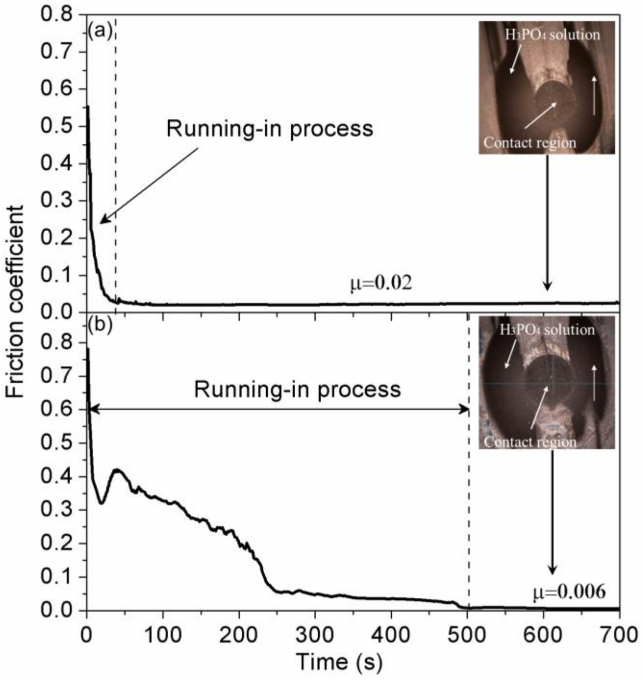

Fig. 7 (a) Evolution of friction coefficient with time under the lubrication of H_3PO_4 solution (pH=0) with an initial volume of 0.5 μL. (b) Evolution of friction coefficient with time under the lubrication of H_3PO_4 solution (pH=2) with an initial volume of 30 μL. The figure inside is the optical images of contact region at the moment of 600 s.

Comparing with Fig. 7(a) and Fig. 7(b), it can be seen that the running-in period for pH=0 is much shorter than that for pH=2. In our previous work, it is found that the running-in process is very important for superlubricity.[25] If there is no running-in process, the superlubricity cannot be obtained even with the lubrication of H_3PO_4 solution with pH=1.5. Therefore, it can be inferred that the running-in period for pH=0 is too short to obtain superlubricity. To confirm whether it is the real reason why the superlubricity cannot be obtained when pH=0, an experiment was designed as follows. First, we used the H_3PO_4 solution with pH=1.5 as lubricant. Second, we measured the friction coefficient for a short period (T_s), and then stopped the measurement. Third, we waited for measurement until there is no fluid liquid left on the substrate (a transparent solid-like film is formed on the substrate instead) due to the evaporation of water in the solution. After that, the friction coefficient was measured again under the same test condition (the load is 3N and the rotation speed is 180 rpm). In this case, the running-in period can be controlled by adjusting the length of T_s. Here, we chosen four different T_s; they are 15 s, 50 s, 100 s, and 200 s. The friction coefficients with the four different T_s are shown in Fig. 8. It is found that when T_s=15 s, the final friction coefficient after the waiting period is 0.035. With the increase of T_s, the final friction coefficient after the waiting period becomes lower. When T_s increases to 100 s, the final friction coefficient becomes 0.011. And when T_s increases to 200 s, the superlubricity (μ=0.004) can be achieved. These results indicate that the final friction coefficient reduces with the running-in period increasing. Only when the running-in period is long enough, can the superlubricity be obtained. Therefore, it can be concluded that the superlubricity cannot be obtained when pH=0 is because the running-in period is too short.

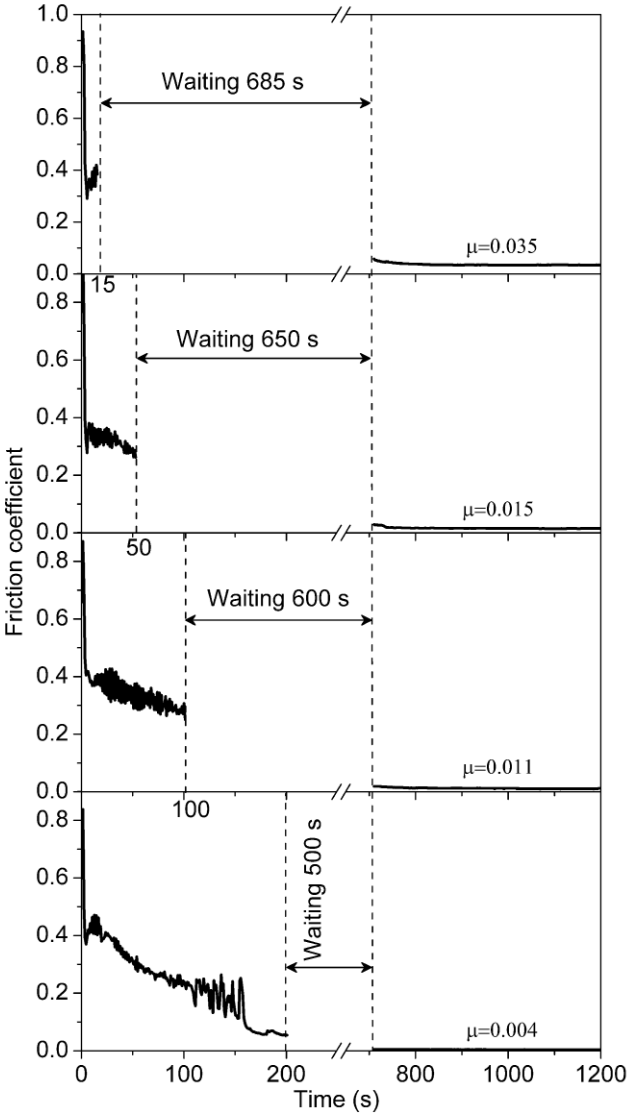

Fig. 8 Evolution of friction coefficient with time under the lubrication of H_3PO_4 solution (pH=1.5) for four different T_s (15 s, 50 s, 100 s, and 200 s)

Why the length of running-in period has influence on superlubricity? During the running-in period, the contact area between two friction surfaces would increase with time due to the original surface layer being ground off by mechanical action. Fig. 9(a) gives the relationship between diameter of contact region and test time with the lubrication of H_3PO_4 solution (pH=1.5). It is found that the diameter of contact region increases from 160 μm to 258 μm with test time increasing from 4 s to 160 s, corresponding to an average pressure reducing from 149 MPa to 57 MPa. When the running-in period is very short, the contact pressure would become high enough to exceed the maximal bearing pressure of the hydrogen bond network composed by H_3PO_4 and H_2O molecules. In this case, the hydrogen bond network would be destroyed and instead there would appear direct asperity contact (dry friction), which would cause a high friction due to the high shearing strength of solid-solid contact. It is consistent with the phenomenon that the friction coefficient becomes high with applied load increasing. For comparing, the diameter of wear region after the lubrication of H_3PO_4 solution with different pH values was measured, as shown in Fig. 9(b). It is found that the diameter of contact region increases from 170 μm to 268 μm with pH value increasing from 0 to 2, which would lead to the average contact pressure reducing from 132 MPa to 53 MPa. As for pH=0 and 0.5, the contact pressure is about 132 MPa and 92 MPa, which is equal to the contact pressure when the running-in period is 10 s and 24 s for pH=1.5, respectively. Therefore, it can be concluded that the high contact pressure for pH=0 and pH=0.5 is one of the main reason why the superlubricity cannot be achieved.

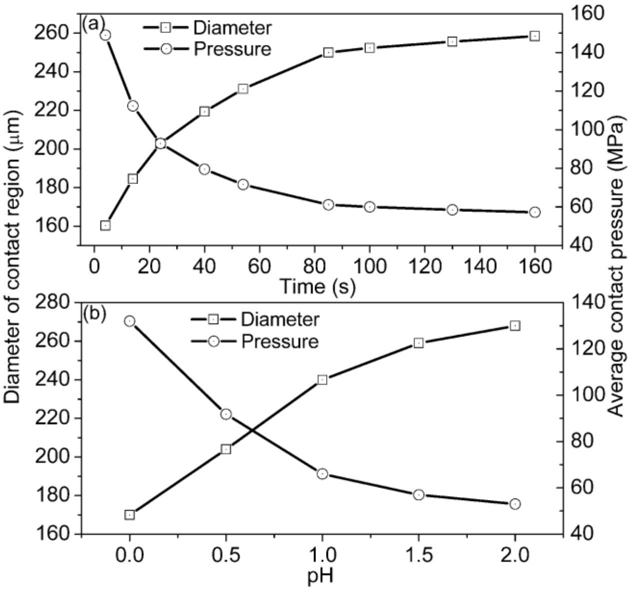

Fig. 9 (a) Relationship between diameter of wear region (contact pressure) and test time with the lubrication of H_3PO_4 solution (pH=1.5). (b) Relationship between diameter of wear region (contact pressure) and pH value of H_3PO_4 solution.

In the meantime, our previous work indicates that the running-in process of superlubricity includes two parts; they are tribochemical reaction between hydrogen ions and friction surfaces and forming hydrogen bond network between H_3PO_4 and H_2O molecules.[27] At the early stage of test, with the effect of rubbing, the hydrogen ions can be adsorbed on the friction surfaces by tribochemical reaction ($SiOH+H^+ \rightarrow SiOH_2^+$, $SiO^-+2H^+ \rightarrow SiOH_2^+$) to form the stern layer and the electrical double layer. After that, with the evaporation of free water in the solution, a thin film with hydrogen bond network would be formed between two surfaces finally, which would lead to the friction coefficient reducing further to 0.004. If there is no running-in period, there would be no rubbing action. In this case, the tribochemical reaction between hydrogen ions and friction surfaces would not occur. Thus there is only a thin film with hydrogen bond network formed between two friction surfaces, which is the reason why the superlubricity cannot be achieved. Similarly, when the running-in period is very short for pH=1.5, there is not enough time for the tribochemical reaction between hydrogen ions and friction surfaces due to the short period of rubbing action, which can also lead to a high friction (Fig. 8). As for pH=0, the friction coefficient reduces to 0.02 very fast (Fig. 7), which indicates that the thin film with the hydrogen bond network is formed very fast. In this case, the two surfaces are separated apart by the hydrogen bond network in a very short period (only 35 s), and thereby there is not enough time for the tribochemical reaction between hydrogen ions and friction surfaces (the period of rubbing action is too short). As a result, there is only a thin film with hydrogen bond network formed between two surfaces, which is in accordance with the final friction state when the running-in period is very short for pH=1.5. From this, it can be concluded that there is not enough time for the tribochemical reaction between hydrogen ions and friction surfaces is also one of the main reason why the superlubricity cannot be achieved when pH=0.

According to the analysis above, it can be found that the too short running-in period can lead to two negative factors for superlubricity; that is high contact pressure and no time for tribochemical reaction, which are the two essential reasons why the superlubricity cannot be obtained when pH is lower than 0.75. Therefore, if we want to obtain superlubricity when pH is lower than 0.75, we have to increase the running-in period to reduce the final contact pressure and meantime to provide the condition for the tribochemical reaction between hydrogen ions and friction surfaces. It is found that the length of running-in period is mainly dependent on the pH value of H_3PO_4 solution and the volume of solution.[24] When the pH is higher and the volume is larger, the running-in period becomes longer. As for pH=0, there is only one way to increase its running-in period; that is increasing the volume of lubricant. However, it is incompatible to forming the lubricating state of starvation. Therefore, it can be concluded that the superlubricity cannot be obtained when pH=0, no matter how to change the test condition. As for pH=2, as long as we increase the volume of lubricant to a certain value that there are enough amounts of H_3PO_4 molecules left in the contact region to form the starvation state, the superlubricity can be achieved.

Conclusion

In summary, we have shown that the superlubricity can be achieved when the pH value of H_3PO_4 solution is in the range of 0.75-2. When pH is less than 0.75, the running-in period is so short that the contact pressure is very high and meantime the tribochemical reaction between hydrogen ions and friction surfaces cannot occur, which is the main reason why the superlubricity cannot be achieved. When pH is greater than 2, the friction surfaces cannot become positively charged to form the stern layer due to the low concentration of hydrogen ions, which is the reason why the friction coefficient keeps a high value. When pH is in the range of 0.75-2, the superlubricity can be obtained as long as the amount of H_3PO_4 molecules in the contact region is large enough to form the starvation state. These results show that the superlubricity is not only closely linked to the concentration of hydrogen ions, but it is also related to the amount of H_3PO_4 molecules in the contact region simultaneously, which is very useful for us to understand the mechanism of liquid superlubricity better.

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