

Investigations of the superlubricity of sapphire against ruby under phosphoric acid lubrication

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Abstract: In this study, we address the superlubricity behavior of sapphire against ruby (or sapphire against itself) under phosphoric acid solution lubrication. An ultra-low friction coefficient of 0.004 was obtained under a very high contact pressure, with a virgin contact pressure up to 2.57 GPa. Related experiments have indicated that the load, sliding speed, and humidity of the test environment can affect superlubricity to some degree, so we tested variations in these conditions. When superlubricity appears in this study a thin film is present, consisting of a hydrogen bond network of phosphoric acid and water molecules adsorbed on the two friction surfaces, which accounts for the ultra-low friction. Most significantly, the wear rate of the sapphire and ruby in the friction process is very slow and the superlubricity state is very stable, providing favorable conditions for future technological applications.

Keywords: friction; superlubricity; sapphire; aqueous lubrication

1 Introduction

Since the 1990s when the term superlubricity was coined [1], it has been used to describe the physical phenomenon that the friction force between two surfaces is very small. Usually, when the ratio of friction force to load in a sliding system is less than 0.01, it is referred to as being in a state of superlubricity [2]. Superlubricity is beneficial for saving energy and reducing wear in mechanical systems, so it has attracted a great amount of attention among tribology researchers [3–7]. At present, there are two main methods for obtaining superlubricity. The first is to change the properties of the friction surfaces so they have incommensurate contact or interfacial interaction (solid superlubricity). This method is used in manufacturing diamond-like carbon (DLC) film [8], MoS₂ film [9], and CN_x film [10]. The second method is to add a lubricant between the two friction surfaces to

separate them (liquid superlubricity). However, the most common lubricants, various kinds of oil, cannot realize superlubricity due to their high pressure–viscosity coefficients. Water lubricants have greater potential for achieving superlubricity because of their low pressure–viscosity coefficients [11]. Klein et al. obtained superlubricity between two mica surfaces lubricated by a surfactant layer and charged polymers at a nano-scale using a surface force apparatus (SFA) [12–14]. Kato et al. obtained superlubricity between two ceramic surfaces (Si₃N₄/CN_x/SiC) with water lubrication at a macro-scale using a traditional tribometer [15, 16]. Superlubricity has also been achieved using lubricants such as glycerol (between two DLC surfaces) [17, 18], a polymer brush (between two SiO₂ surfaces) [19], and plant mucilage (between two glass surfaces) [20]. In our previous work, we also obtained superlubricity between ceramic (Si₃N₄) and glass surfaces lubricated by a phosphoric acid solution and mixtures of polyhydroxy alcohol and acid solutions [21–23].

However, the contact pressures for the liquid superlubricities mentioned above are not very high (less

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than 1 GPa). There is a question as to whether or not superlubricity can be achieved under much higher contact pressure. Obviously, high pressure has many disadvantages for liquid superlubricity, such as the potential for significant deformation, severe wear, and the lubricant molecules being squeezed out. These challenges have made it very difficult to achieve superlubricity under high pressure. If these three disadvantages can be solved, then the liquid superlubricity under high pressure becomes possible.

Recently, we found that the liquid superlubricity can be achieved even when the initial maximal contact pressure between two friction surfaces reaches up to 2.57 GPa, when using sapphire and ruby (or sapphire against its own) surfaces lubricated by a phosphoric acid solution (pH = 1.5). This superlubricity state is very stable, and can last for more than 9 h. Therefore, in this paper we investigate the superlubricity behavior and mechanism when using these surfaces and this lubricant, and discuss the relationship between the lubrication conditions (load, speed, and humidity) and superlubricity.

2 Experimental section

The friction pairs are a ruby or sapphire ball with a diameter of 5 mm and a sapphire plate with a diameter of 20 mm and a thickness of 3 mm (both obtained from Zhaohong Technology Co. Ltd., China). The surface roughness (R_z) of the ball and plate is about 12 nm. Both the ball and the plate were cleaned in an ultrasonic bath with acetone and ethanol for 15 min sequentially, and then washed with deionized water and dried with compressed air prior to the test. The lubricant, a phosphoric acid (H_3PO_4) solution with a pH value of 1.5 (corresponding to a concentration of 1.6% (w/w)), was prepared by diluting commercial phosphoric acid (obtained from Beijing Chemical Works, purity > 99% and concentration > 85%) with deionized water. Before the friction test, a few droplets of this lubricant (10 μ L) were dripped between the ball and the plate.

The friction coefficient was measured on a Universal Micro-Tribotester (UMT-3, Bruker) using a ball-on-disk model. The load applied on the disk ranged from 0.5 N to 15 N. According to the Hertz contact theory and with regard to the mechanical properties of friction

surfaces (elasticity modulus = 425 GPa, Poisson's ratio = 0.30), the maximal contact pressure is between 0.95 GPa and 2.94 GPa. The rotation speed of the disk ranged from 5 rpm to 1,200 rpm, and the radius of the sliding track on the disk was 3 mm, corresponding to a linear sliding speed of 0.00157 m/s to 0.377 m/s. The ambient temperature was about 25 °C and the relative humidity of the test environment ranged from 10% to 100%. To obtain an accurate friction coefficient value, measuring errors were eliminated by adjusting the disk levelness until the same friction coefficients were obtained in reverse sliding directions (for more details see Ref. [19]) [24].

The topography of the friction surfaces was investigated with a white light interferometer (MICROXAM-3D) and an optical microscope (Olympus). The details of the wear region were investigated with an atomic force microscope (AFM, Nanoman VS). The images were obtained under ambient conditions in tapping mode. The chemical composition of the worn surfaces was measured with a confocal Raman spectrometer (Jobin Yvon HR800). The laser, with a wavelength of 514 nm, was focused on the sample through a 50 \times objective microscope.

3 Results and discussions

Figure 1 shows the evolution of the friction coefficient over time for sapphire against ruby lubricated with an H_3PO_4 solution (pH = 1.5). The friction coefficient is 0.2 at the beginning of test. After about 320 s, the friction coefficient reduced to a value of 0.004, entering the superlubricity regime. Here, the time elapsed from the beginning of the test to the appearance of the lowest friction value is defined as the running-in period. After this 320 s running-in period, the friction coefficient maintains this ultra-low value ($\mu = 0.004$) until the end of the test (2,000 s). The friction coefficient was measured more than ten times, and all the friction curves over time (decreasing during the running-in period and then approaching a steady-state value) are almost identical in every test. We then changed the ruby ball to a sapphire ball, and found that superlubricity can also be obtained using sapphire against sapphire; the resulting friction curve is the same as that for sapphire against ruby. This indicates

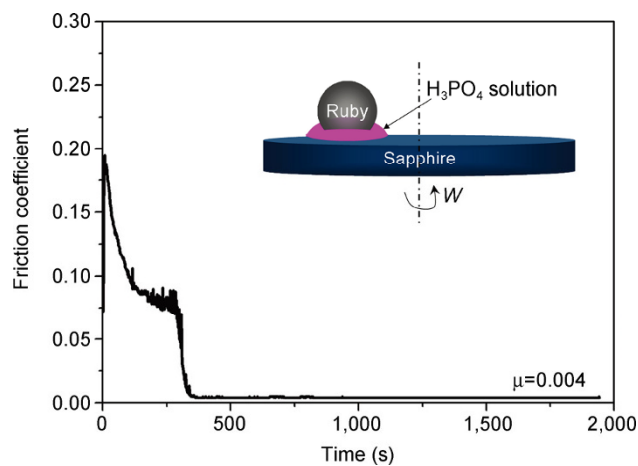


Fig. 1 Friction coefficient over time with the H_3PO_4 solution lubricant (pH = 1.5), with a load of 3 N, a rotation speed of 180 rpm, and humidity at 30%.

that the superlubricity is independent of the chromium (Cr) in the ruby. In addition, we found that the ultra-low friction state ($\mu = 0.004$) can last for more than 9 h, indicating the stability of this superlubricity state.

Next, we studied the effect of speed and applied load on superlubricity, as shown in Figs. 2(a) and 2(b). We found that superlubricity ($\mu < 0.01$) can be obtained when the rotation speed is greater than 15 rpm (sliding speed = 0.00471 m/s). In addition, when the rotation speed is greater than 30 rpm (sliding speed = 0.00942 m/s), the friction coefficient remains nearly constant ($\mu = 0.004$). However, when the rotation speed decreases from 30 rpm to 5 rpm, the friction coefficient increases from 0.004 to 0.017. And when the rotation speed reduces to 5 rpm (sliding speed = 0.00157 m/s), superlubricity ($\mu < 0.01$) can no longer be achieved. With respect to load, we found that the friction coefficient remains nearly constant ($\mu = 0.004$) when the load ranges from 0.5 N to 10 N, but increases when the applied load increases from 10 N to 15 N. When the applied load reaches 15 N, superlubricity ($\mu < 0.01$) can no longer be obtained. From these results, we conclude that when the sliding speed is greater than 0.00942 m/s and the applied load is less than 10 N, changes in speed and load have almost no effect on superlubricity.

To investigate the superlubricity behavior of sapphire against ruby, as observed above, we carried out a series of experiments as follows. At the beginning of test, the H_3PO_4 solution was in a fluid state and was

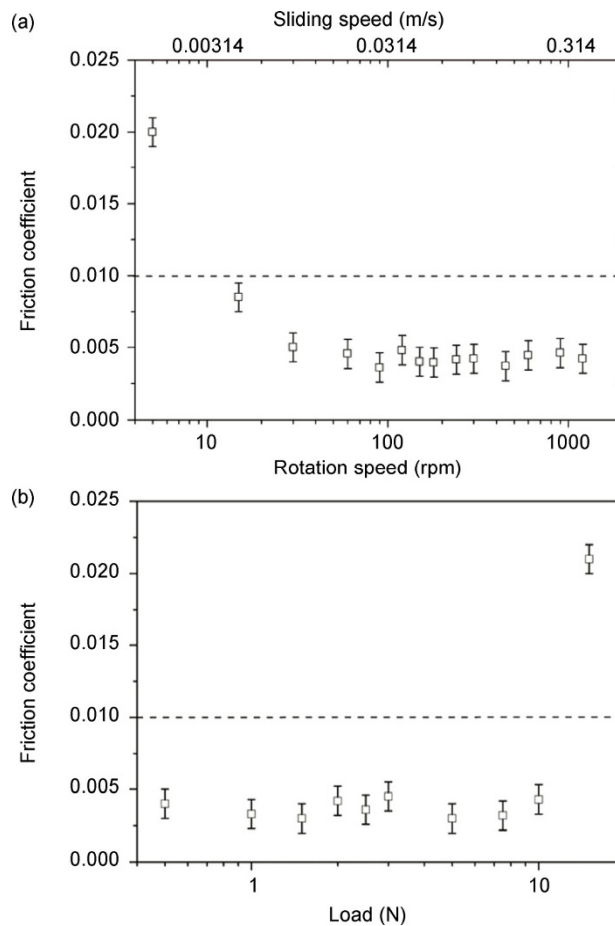


Fig. 2 (a) Lowest friction coefficient when using H_3PO_4 solution lubrication (pH = 1.5) with different rotation speeds, a load of 3 N, and humidity at 30%. (b) Lowest friction coefficient when using H_3PO_4 solution lubrication (pH = 1.5) with different loads, a rotation speed of 180 rpm, and humidity at 30%.

confined between the two friction surfaces. During the running-in period, the free water in the solution was evaporated gradually. When superlubricity appeared, there was almost no fluid remaining on the sapphire plate, and a transparent solid-like film had formed on the plate instead. To observe this film in greater detail, we used the optical microscope to study both the plate and the ball, as shown in Figs. 3(a) and 3(b). We found the thin film to be adsorbed both on the track of the plate and on the top region of the ball. To analyze this thin film's chemical composition, we measured its Raman spectrum, as shown in Figs. 3(c) and 3(d). We observed that the thin film adsorbed on the track had a strong scattering peak at 910 cm^{-1} (with other peaks at 378 cm^{-1} , 417 cm^{-1} , and 643 cm^{-1} that are typical of sapphire bonds), indicating the bond of

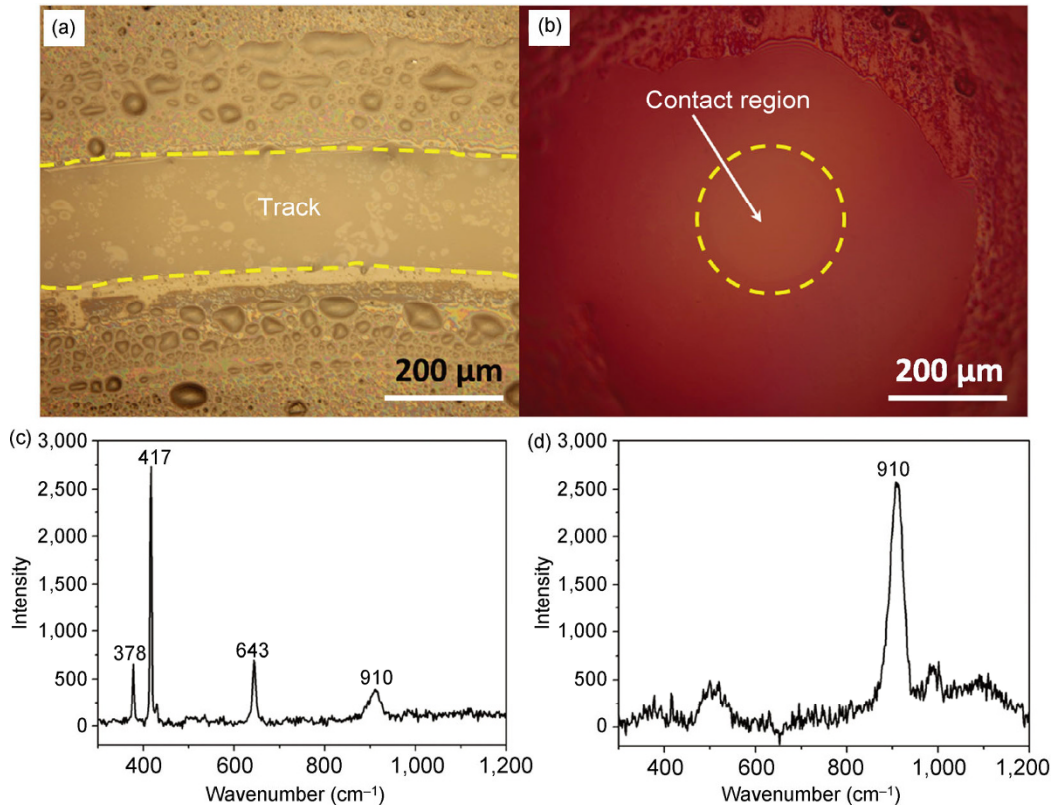


Fig. 3 (a) Optical image of the track on the sapphire plate after the friction test. (b) Optical image of the top region on the ruby ball after the friction test. (c) Raman spectrum of the thin film adsorbed on the track after the friction test. (d) Raman spectrum of the thin film adsorbed on the top region of the ball after the friction test.

the P–OH symmetric stretch of the H_3PO_4 molecule and the H_2PO_4^- ions (by ionization) [25]. A shift to a higher frequency has been observed relative to the typical bond of a P–OH symmetric stretch (890 cm^{-1}) in dilute H_3PO_4 solution [26], which indicates that a strong hydrogen bond effect exists in the film adsorbed on the track [27]. Therefore, we concluded that a hydrogen bond network composed of H_3PO_4 , H_2PO_4^- , and H_2O had formed in the thin film. We also found that the Raman spectrum of the thin film adsorbed on the top region of the ball (910 cm^{-1}) was almost identical to that on the track, indicating the presence of the same thin film with a hydrogen bond network adsorbed on the top region of the ball.

To further investigate the topography of the friction surfaces, we measured both the track on the plate and the top region of the ball using a white light interferometer after washing the adsorbed film with de-ionized water for about 10 min, as shown in Figs. 4(a) and 4(b). We can see a concave track with a width of

$160\text{ }\mu\text{m}$ and a depth of 15 nm on the plate. The depth is so shallow that the track is difficult to identify with the optical microscope. On the top region of the ball, there is a worn flat region with a diameter of $200\text{ }\mu\text{m}$. From these two images, we determined the wear volume of the sapphire and the ruby to be about $4.52 \times 10^{-5}\text{ mm}^3$ and $3.14 \times 10^{-4}\text{ mm}^3$, respectively, with a corresponding wear rate of $2.67 \times 10^{-10}\text{ mm}^3/\text{Nm}$ and $1.85 \times 10^{-9}\text{ mm}^3/\text{Nm}$, respectively. These results indicate that the wear rates of sapphire and ruby is much lower than the wear rates of ceramics (10^{-8} – $10^{-6}\text{ mm}^3/\text{Nm}$) with water lubrication [28].

To study the friction surfaces in greater detail, both the track on the plate and the worn region of the ball were observed under an AFM, as shown in Figs. 5(b) and 5(c). We found many shallow micro-grooves along the sliding direction on the track surface. From Fig. 5(e), it can be seen that the width of the grooves is several micrometers and the depth is several nanometers. Compared with the original surface of the

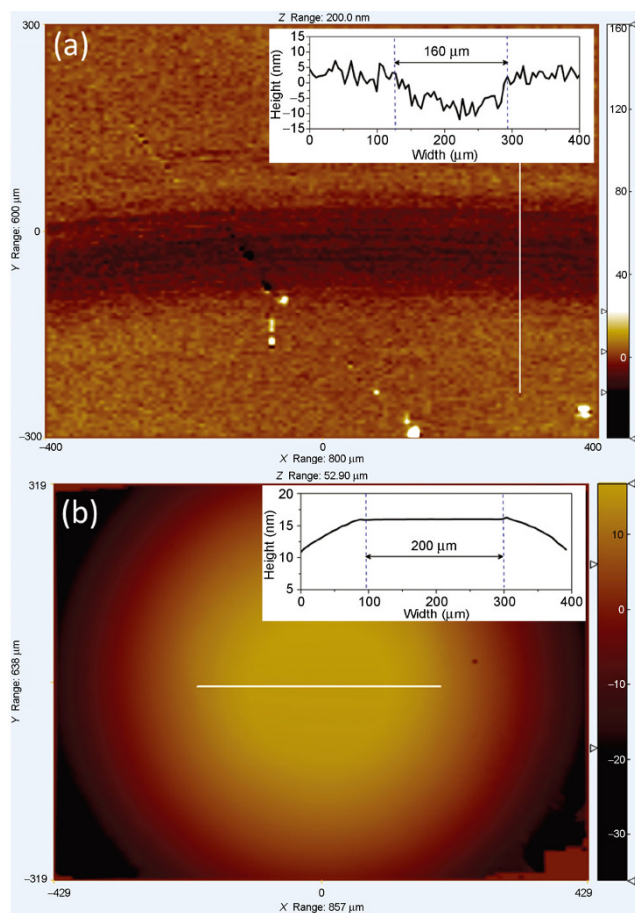


Fig. 4 (a) Topography of the track on the plate. (b) Topography of the top region of the ball.

sapphire (Fig. 5(a)), the surface roughness (R_z) increases from 0.486 nm to 5.506 nm, indicating that the rubbing surface becomes much rougher when superlubricity appears. On the worn region of the ball, there are also some shallow micro-grooves along the sliding direction. In addition, there are many nano-particles of different sizes adsorbed onto the worn region of the ball, which are the abrasive particles from the worn surfaces. From these results, we infer that the micro-grooves on the rubbing surfaces are produced by the plowing effect of these nano-particles between the two surfaces during the running-in process.

As mentioned above, there is a thin film with a hydrogen bond network of H_3PO_4 , H_2PO_4^- , and H_2O molecules between the two friction surfaces when superlubricity appears. It can be inferred that if excess free water is introduced in the contact region, it would destroy the hydrogen bond network by breaking the equilibrium state between the H_3PO_4 and H_2O molecules, which would then lead to high friction. To confirm this inference, different volumes of deionized water (1 μL , 3 μL , and 5 μL) were added to the track when the friction coefficient reached its lowest value, as shown in Fig. 6. We found that the friction coefficient becomes suddenly high (from 0.004 to 0.07) once deionized water is introduced. However, superlubricity can be restored after a short running-in period. In

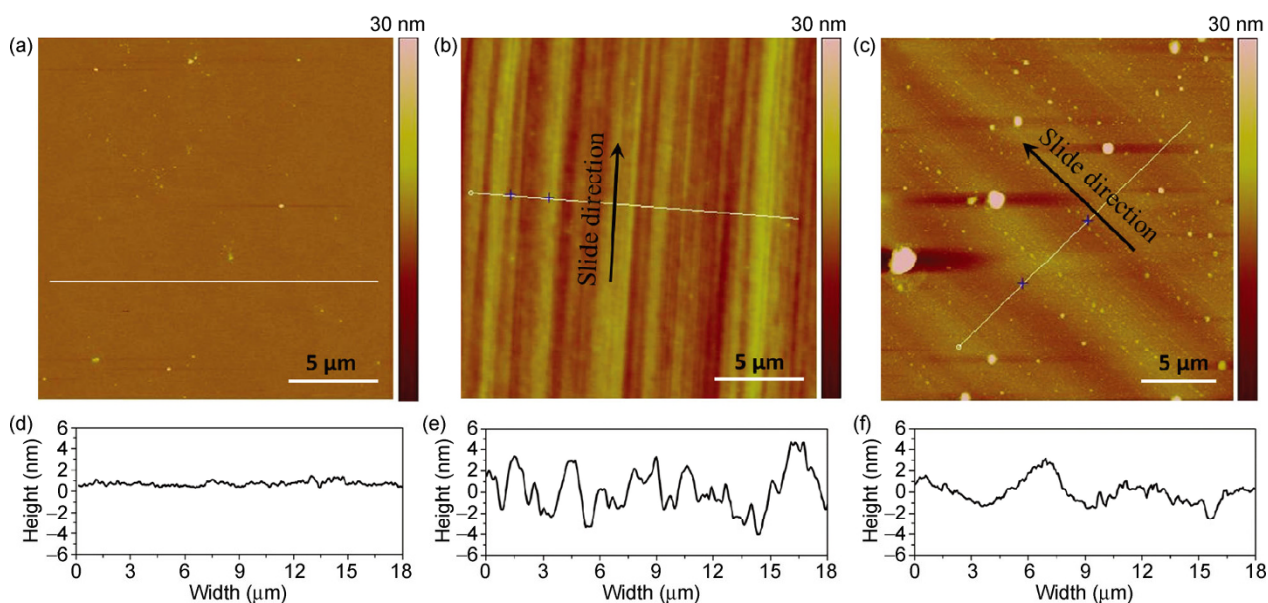


Fig. 5 (a) AFM image of the original surface of the sapphire. (b) AFM image of the track on the surface of the sapphire. (c) AFM image of the worn region on the ruby ball. (d) Cross-sectional profile (white line in (a)) of the original surface of the sapphire. (e) Cross-sectional profile (white line in (b)) of the track on the surface of the sapphire. (f) Cross-sectional profile (white line in (c)) of the worn region on the ruby ball.

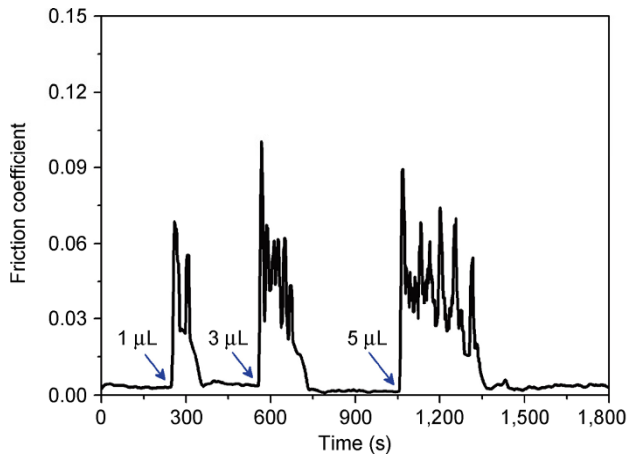


Fig. 6 Friction coefficient with the H_3PO_4 solution (pH = 1.5) lubrication after adding different volumes of deionized water (1 μL , 3 μL , and 5 μL) to the track, with a load of 3 N, a rotation speed of 180 rpm, and humidity at 30%.

addition, the running-in period becomes longer as the volume of deionized water increases (106 s for 1 μL , 173 s for 3 μL , and 312 s for 5 μL). This is because excess deionized water requires a longer evaporation period from the contact region as the volume of water becomes larger. Once the excess deionized water has evaporated completely (the mass of the remaining solution on the plate remains constant), the hydrogen bond network can be restored and superlubricity can again be achieved. Therefore, we conclude that superlubricity is closely related to the hydrogen bond network adsorbed on the two friction surfaces.

According to this phenomenon, we can infer that humidity probably does affect superlubricity, because high humidity indicates the presence of water vapor in the air, which can then interfere with the hydrogen bond network and destroy the equilibrium state between the existing H_3PO_4 and H_2O molecules. To verify this inference, the humidity of the test environment was changed from 10% to 100% when superlubricity appeared. The friction results at different humidities are shown in Fig. 7. We found that when the humidity is less than 70%, changes in humidity had almost no effect on superlubricity (the friction coefficient remains at 0.004). However, when the humidity increased from 70% to 100%, the friction coefficient increased from 0.004 to 0.018. When humidity increased to 85%, superlubricity ($\mu < 0.01$) could not be obtained. This is because the water vapor can easily enter the hydrogen

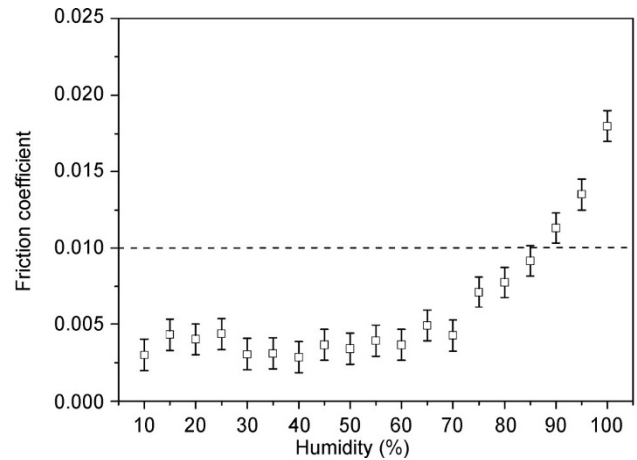


Fig. 7 Relationship between humidity and the friction coefficient with H_3PO_4 solution lubrication, at a load of 3 N and a rotation speed of 180 rpm.

bond network when there is a high content of water vapor in the air. Thus we verified that when high humidity occurs, the hydrogen bond network of the H_3PO_4 , H_2PO_4^- , and H_2O molecules can be destroyed, leading to high friction, in accordance with the phenomenon seen in Fig. 6. However, when the humidity is not high (less than 70%), the water vapor in the air cannot easily enter the hydrogen bond network. Neither can the water molecules in the hydrogen bond network easily evaporate from the network, due to the moisture retention tendency of phosphoric acid molecules. Therefore, when humidity is in the range of 10%–70%, the equilibrium state between H_3PO_4 and H_2O remains constant, so the friction coefficient also remains constant.

What causes superlubricity? In our previous work, we found two preconditions for superlubricity: first that hydrogen ions be adsorbed on friction surfaces and second that a hydrogen bond network be formed between two surfaces [29, 22]. As for sapphire and ruby, if they are immersed in a strong acid solution (pH < 4.1), hydrogen ions can be adsorbed on their surfaces by a protonation reaction ($\text{AlOH} + \text{H}^+ \rightarrow \text{AlOH}_2^+$, $\text{Al}_2\text{OH} + \text{H}^+ \rightarrow \text{Al}_2\text{OH}_2^+$) because there are so many Al–OH bonds on the surfaces of sapphire and ruby [30]. Therefore, during the running-in period, the hydrogen ions in the phosphoric acid solution can be adsorbed on the surfaces of sapphire and ruby, which can lead to the two surfaces becoming positively charged. This results in the formation of a stern layer

and an electrical double layer on the two friction surfaces that reduce the friction force. In addition, a hydrogen bond network among the H_3PO_4 , H_2PO_4^- , and H_2O molecules also forms on the two friction surfaces (Figs. 3(c) and 3(d)). Therefore, the superlubricity occurring between sapphire and ruby satisfies the two preconditions for superlubricity stated above. We can conclude that the mechanism of superlubricity between sapphire and ruby is attributable to the formation of the hydrogen bond network between the phosphoric acid and water molecules on the stern layer (induced by hydrogen ions) after the running-in period [29].

With regard to the relationship between rotation speed and the friction coefficient, we can infer that the friction pairs are present in the mixed lubrication when superlubricity appears. As shown in Figs. 5(b) and 5(c), the contact surface is not very smooth ($R_z = 5.506 \text{ nm}$) so we can infer the probability of direct asperity contact. We believe there to be three kinds of contact models in the contact region, as shown in Fig. 8. The first is the hydrogen bond network contact, which can be affected by the load and rotation speed due to the hydrodynamic effect between the two sliding surfaces. The second kind is the stern layer contact, which originates from the strong adsorption of hydrogen ions on the friction surface. The third is the direct contact, which occurs when the stern layer is destroyed by high contact pressure. When the sliding speed is high (more than 0.00942 m/s), the hydrogen bond network bears most of the load and plays the primary role in reducing friction. In this case, the

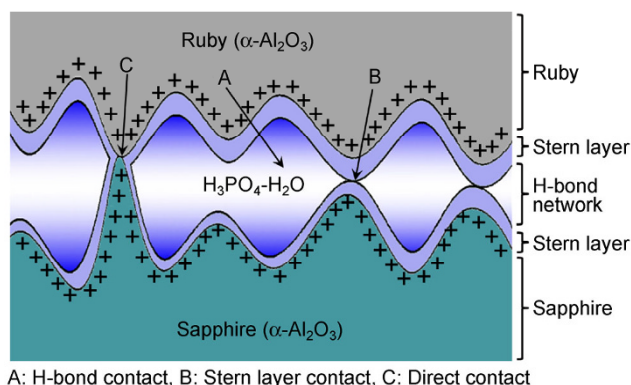


Fig. 8 Schematic illustration of the contact region between the two friction surfaces (ruby and sapphire).

relative proportion of stern layer contact is very small so there is almost no direct asperity contact. Because the shearing strength between hydrogen bond networks and the stern layers is very low (forming a hydrated water layer) [31], this leads to ultra-low friction. But when the speed is low (less than 0.00471 m/s), the bearing pressure on the hydrogen bond network reduces due to the reduction in the hydrodynamic effect, which then leads to an increase in the bearing pressure on the stern layer. When the bearing pressure on the stern layer is so high that the stern layer is destroyed, direct asperity contact occurs, which then leads to high friction due to the high shearing strength associated with direct asperity contact. With respect to load, when it is less than 10 N , the hydrogen bond network and the stern layer can bear the load, so there is no direct asperity contact, which can lead to ultra-low friction. But when the load is more than 15 N , the contact pressure is so high that the hydrogen bond network and the stern layer can be destroyed, which leads to direct asperity contact and high friction. Therefore, when the sliding speed is lower than 0.00471 m/s and the load becomes higher than 15 N , the proportion of direct asperity contact increases, resulting in an increasing friction coefficient.

Compared to the superlubricity that occurs between Si_3N_4 and glass lubricated by phosphoric acid [21], the maximal contact pressure between sapphire and ruby (2.57 GPa) is much higher than that between Si_3N_4 and glass (0.7 GPa). How is superlubricity achieved using phosphoric acid lubrication under such high pressure? As mentioned in the introduction, high pressure usually leads to significant deformation, severe wear, and the lubricant molecules being squeezed out, all of which impede the formation of superlubricity. The key to achieving superlubricity under high pressure is the excellent surface properties of sapphire and ruby. Both have a high elastic modulus, hardness, and durability under hard wear. When they are in contact with each other, their deformation is very small; the diameter of the contact region is about $67 \mu\text{m}$ under a load of 3 N . According to our white light interferometer images (Figs. 4(a) and 4(b)), the wear is also very minor. The hydrogen bond network adsorbed on the two friction surfaces prevents the phosphoric acid molecules from being easily squeezed

out even under a high pressure, due to the strong adsorption of hydrogen ions on the surfaces of sapphire and ruby by a protonation reaction. It is thus clear that the excellent surface properties of sapphire and ruby provide favorable conditions for achieving superlubricity under a high pressure. Using friction pairs other than sapphire and ruby that do not have the same surface properties, it is very difficult to obtain superlubricity with phosphoric acid solution lubrication under such high pressure.

4 Conclusion

In summary, this study investigated the superlubricity behavior of sapphire against ruby (or sapphire against itself) using phosphoric acid solution lubrication. The resulting ultra-low friction is attributed to the formation of a hydrogen bond network on the stern layer induced by hydrogen ions. We found the superlubricity state to be very stable when the load is in the range of 0.5 N to 10 N, the sliding speed is in the range of 0.00942 m/s to 0.377 m/s, and the humidity of the test environment is in the range of 10% to 70%. Moreover, the degree of wear to the sapphire and ruby that occurs during the running-in period is also very small. These excellent friction properties point to the potential application of phosphoric acid solution in the lubrication of sapphire bearing under high pressure, which would not only greatly reduce the consumption of friction energy, but also provide nearly wear-free conditions in the lubrication system.

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Reference

- [1] Hirano M, Shinjo K. Atomistic locking and friction. *Phys Rev B* **41**(17): 11837–11851 (1990)
- [2] Erdemir A, Martin J-M. *Superlubricity*. New York (USA): Elsevier, 2007.
- [3] Luo J B, Lu X C, Wen S Z. Developments and unsolved problems in nano-lubrication. *Prog Nat Sci* **11**(3): 173–183 (2001)
- [4] Ma Z-Z, Zhang C-H, Luo J-B, Lu X-C, Wen S-Z. Superlubricity of a Mixed Aqueous Solution. *Chin Phys Lett* **28**(5): 056201 (2011)
- [5] Hu Y, Ma T, Wang H. Energy dissipation in atomic-scale friction. *Friction* **1**(1): 24–40 (2013)
- [6] Li J J, Luo J B. Advancements in superlubricity. *Sci China Tech Sci* **56**(12): 1–11 (2013)
- [7] Luo J B, Wen S Z, Li L K Y, Wong P L. Progresses and problems in nano-tribology. *Chin Sci Bull* **43**(5): 369–378 (1998)
- [8] Erdemir A. Genesis of superlow friction and wear in diamondlike carbon films. *Tribol Int* **37**(11–12): 1005–1012 (2004)
- [9] Martin J M, Donnet C, Lemogne T, Epicier T. Superlubricity of molybdenum-disulfide. *Phys Rev B* **48**(14): 10583–10586 (1993)
- [10] Kato K, Umehara N, Adachi K. Friction, wear and N₂-lubrication of carbon nitride coatings: A review. *Wear* **255**(11): 1062–1069 (2003)
- [11] Raviv U, Laurat P, Klein J. Fluidity of water confined to subnanometre films. *Nature* **413**(6851): 51–54 (2001)
- [12] Raviv U, Giasson S, Kampf N, Gohy J F, Jerome R, Klein J. Lubrication by charged polymers. *Nature* **425**(6954): 163–165 (2003)
- [13] Briscoe W H, Titmuss S, Tiberg F, Thomas R K, McGillivray D J, Klein J. Boundary lubrication under water. *Nature* **444**(7116): 191–194 (2006)
- [14] Klein J. Hydration lubrication. *Friction* **1**(1): 1–23 (2013)
- [15] Chen M, Kato K, Adachi K. Friction and wear of self-mated SiC and Si₃N₄ sliding in water. *Wear* **250**: 246–255 (2001)
- [16] Zhou F, Adachi K, Kato K. Sliding friction and wear property of a-C and a-CN_x coatings against SiC balls in water. *Thin Solid Films* **514**(1–2): 231–239 (2006)
- [17] Bouchet M I D B, Matta C, Le-Mogne T, Martin J M, Zhang Q, Goddard W A, III, Kano M, Mabuchi Y, Ye J. Superlubricity mechanism of diamond-like carbon with glycerol. Coupling of experimental and simulation studies. *J Phys Conference Series* **89**: 012003 (2007)

- [18] Matta C, Joly-Pottuz L, Bouchet M I D, Martin J M. Superlubricity and tribochemistry of polyhydric alcohols. *Phys Rev B* **78**(8): 085436 (2008)
- [19] Drobek T, Spencer N D. Nanotribology of surface-grafted PEG layers in an aqueous environment. *Langmuir* **24**(4): 1484–1488 (2008)
- [20] Li J J, Liu Y H, Luo J B, Liu P X, Zhang C H. Excellent lubricating behavior of braseniaschreberi mucilage. *Langmuir* **28**(20): 7797–7802 (2012)
- [21] Li J J, Zhang C H, Luo J B. Superlubricity behavior with phosphoric acid-water network induced by rubbing. *Langmuir* **27**(15): 9413–9417 (2011)
- [22] Li J J, Zhang C H, Ma L R, Liu Y H, Luo J B. Superlubricity achieved with mixtures of acids and glycerol. *Langmuir* **29**(1): 271–275 (2013)
- [23] Li J J, Zhang C H, Luo J B. Superlubricity achieved with mixtures of polyhydroxy alcohols and acids. *Langmuir* **29**(17): 5239–5245 (2013)
- [24] Li J J, Zhang C H, Sun L, Luo J B. Analysis of measurement inaccuracy in superlubricity tests. *Tribol Trans* **56**(1): 141–147 (2013)
- [25] Preston C M, Adams W A. Laser Raman-spectroscopic study of aqueous ortho-phosphate salts. *J Phys Chem* **83**(7): 814–821 (1979)
- [26] Adams W A, Preston C M, Chew H A M. High-pressure conductivity and laser Raman-spectroscopic study of aqueous ortho-phosphate solutions at 25 °C. *J Chem Phys* **70**(5): 2074–2080 (1979)
- [27] Kameda Y, Sugawara K, Hosaka T, Usuki T, Uemura O. Hydrogen-bonded structure in concentrated aqueous phosphoric acid solutions. *Bull Chem Soc Jpn* **73**(5): 1105–1112 (2000)
- [28] Zhou F, Wang X L, Kato K J, Dai Z D. Friction and wear property of a-CN_x coatings sliding against Si₃N₄ balls in water. *Wear* **263**: 1253–1258 (2007)
- [29] Li J J, Zhang C H, Sun L, Lu X C, Luo J B. Tribochemistry and superlubricity induced by hydrogen ions. *Langmuir* **28**(45): 15816–15823 (2012)
- [30] Fitts J P, Shang X M, Flynn G W, Heinz T F, Eiseenthal K B. Electrostatic surface charge at aqueous/alpha-Al₂O₃ single-crystal interfaces as probed by optical second-harmonic generation. *J Chem Phys* **109**(16): 7981–7986 (2005)
- [31] Raviv U, Klein J. Fluidity of bound hydration layers. *Science* **297**(5586): 1540–1543 (2002)



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