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Formation of metal–F bonds during frictional sliding: Influence of water and applied load

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ABSTRACT

Effects of water lubrication and applied load on the formation of PTFE transfer films and metal–F bonds during sliding when PTFE filled composites sliding against steel and Al_2O_3 are investigated. In water-lubricated conditions, XPS analysis reveals that a thin layer of water molecules at the sliding interface inhibits the formation of PTFE transfer films and Al–F bonds on the Al_2O_3 ball, leading to a detrimental effect on the tribo-performance. Under various normal loads in dry sliding condition, it is found that the smearing of PTFE onto the wear surface of the composite and the transfer of PTFE onto the surface of the steel counterpart are stimulated by a high load. During sliding, the contact pressure is found to be the driving force of the reaction between steel and PTFE. It is concluded that under various loads, the total amount of PTFE transfer films has a larger impact on the friction behavior than the formation of Fe–F bonds.

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1. Introduction

Polytetrafluoroethylene (PTFE) filled composites are widely used in dry sliding bearings, due to the self-lubricating and maintenance-free properties. Several decades ago Tabor et al. have already examined effects of the formation mechanism, thickness and stability of PTFE transfer films on the counterparts to the tribo-performance of PTFE or PTFE filled composites [1,2]. Nevertheless, the importance of the formation of chemical bonds during the sliding process was not examined. Much later XPS analysis indicated the formation of metal–fluoride bonds on the steel or other metal surfaces [3–5], without linking the chemical reactions to the tribo-performance. In our previous study it was found that the formation of metal–fluoride (metal–F) bonds enhances the tribo-performance of PTFE filled composites, especially in the case of having insufficient PTFE transfer films [6]. Al_2O_3 balls performed much better than Si_3N_4 balls when sliding against a SiO_2 -epoxy composite with 7.5 wt.% PTFE, which was attributed to the formation of Al–F bonds.

When sliding in water-lubricated conditions, Krick et al. [7] and Mens et al. [8] measured a lower coefficient of friction (CoF) but a higher wear rate of PTFE-based composites in a water submerged

experiment than in dry conditions. The detrimental effect of water on the wear performance of polymer composites was attributed mainly to the inhibition of transfer-film formation [9–11]. However, Jia et al. found that the wear rate and the friction coefficient of PTFE-based composites were lower in water-lubricated sliding than that under dry sliding, due to the water boundary lubrication [12]. The role of water lubrication on the tribo-performance of PTFE filled composites could be different in different sliding systems and conditions. To the best of our knowledge the effect of water on the formation of metal–F bonds during sliding has not been studied before in detail.

The influence of loading conditions on the CoF of PTFE-based composites has also been extensively reported in literature. Most of the research has concluded that the CoF decreases with increasing load [13–16]. Kragelskii explained such a behavior by the elastic deformation of the surface asperities [17]. However, the role of applied load, or more specifically the contact pressure, on the formation of metal–F bonds was not examined experimentally.

This work is aimed at scrutinizing the effect of water lubrication and normal load on the formation of PTFE transfer films and metal–F bonds during sliding when PTFE filled composites sliding against steel and Al_2O_3 balls. It will be shown that this study leads to a better understanding of the formation of PTFE transfer film and the formation of metal–F bonds under various sliding conditions.

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2. Experiments

2.1. PTFE/SiO₂/epoxy composite

The epoxy- and SiO₂-containing powder, Epomet F, was purchased from Buehler GmbH. The powder is mainly composed of about 31 ± 2 wt.% epoxy resin (CAS: 26265-08-7) and about 65 ± 2 wt.% SiO₂ particles (20–100 μm). It also contains 1–3 wt.% 2,4,6-tris(dimethylaminomethyl)phenol, 1–2 wt.% antimony oxide (Sb₂O₃) particles (for flame retardant property) and less than 1 wt.% carbon black (pigment). The PTFE powder, Zonyl MP 1000 fluoro-additive, was purchased from DuPont. After mechanically mixing the two powders for 30 min, the mixed powder was cured at about 160 °C for 20 min under 0.41 MPa pressure and cooled down with water cooling. The details of the PTFE/SiO₂/epoxy composites were discussed in our previous paper [18].

The PTFE/SiO₂/epoxy composite is referred to as the 'Epomet-PTFE composite'. For the sake of conciseness, the Epomet-PTFE composite is named as 'Epomet-PTFExx', where xx denotes the weight percentage of the PTFE. The measured average Vickers hardness of the cured pure Epomet composite (without PTFE) and the Epomet-PTFE12.5 composite are around 97 and 55 HV_{0.6}, respectively. Such a hard Epomet-PTFE12.5 composite is believed to be advantageous to form a thin PTFE transfer film on the sliding counterpart ball, and study the formation of metal–F bonds underneath the transfer film.

2.2. Tribological tests

The friction and wear behavior of the composites against two kinds of counterpart balls were studied using a ball-on-disk tribometer under dry sliding condition and in water-lubricated condition. Ø13 mm 100Cr6 bearing steel balls were mainly used as the counterparts balls. In the case of studying the effects of water, Al₂O₃ balls were used to exclude the influence of corrosion (rusting). The surface roughness (Ra) values of these balls were measured to be around 54 nm with confocal microscopy (60 μm cutoff, 705 × 728 μm image size, the same for the rest Ra in this work). The density of the 100Cr6 steel and the Al₂O₃ balls are 7.8 and 3.9 g/cm³, respectively. During sliding tests the counterpart ball was stationary. The standard sliding conditions were 60 N load, velocity of 2 cm/s, 35 ± 2% relative humidity and room temperature (22 ± 2 °C). To study the effect of various sliding conditions, in each test only one experimental parameter was varied and the others remained unchanged. The normal load was set ranging between 0.1 N and 60 N. The relative humidity was adjusted with a feedback controlled flux of dry air or water vapor into the protection box. Water lubrication tests were performed with the sliding interface being immersed in distilled water. No evident increase of temperature in the sliding interface in the dry sliding conditions is measured after sliding for 100 m at sliding velocity of 2 cm/s.

To study the role of fluoridation of Al₂O₃ on its friction performance, the Al₂O₃ ball was immersed into hydrofluoric acid (2%) for 16 h. Then, it was rinsed with distilled water and acetone (3 times), and dried before being used in tribo-tests.

2.3. Characterization of the wear surface

After the tribo-tests, the morphology of the wear surfaces of the Epomet-PTFE composites and of the balls were inspected using light microscopy and scanning electron microscopy (SEM, Philips XL-30 FEG ESEM). For SEM observation, a thin Au layer was applied on the surface of the Epomet-PTFE composites and the Al₂O₃ ball so as to avoid charging.

Confocal microscopy (Nanofocus μSurf) was used to measure the surface profile of the wear surfaces of the composites and

the balls, for the assessment of the wear volume with a self-programmed Matlab code with a margin of error of ±5%. For the composites, areas slightly away from wear tracks were taken as the original surface, to calculate the wear volumes. For the balls, original ball surfaces measured before tests were used to compare with worn surfaces after tests. For the balls with an average wear depth less than 1.5 μm, the mean deviation of wear volume estimated with the code is less than ±30%. For the calculation of the wear volume of the composites, the average values were obtained with at least two tests after sliding for 1000 m and 4 confocal scans each test, if not specified otherwise.

XPS analysis was performed to investigate the elemental composition and possible chemical bonds on the wear surfaces of the balls, using a Surface Science SSX-100 ESCA instrument with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV). During data acquisition, the pressure in the measurement chamber was kept below 2×10^{-7} Pa. The diameter of the analyzed area was 600 μm. Freshly tested ball samples (after 100 m sliding) were used for all the measurements. The electron takeoff angle with respect to the normal to the horizontal plane was 37°, while the wear scars of the steel balls were always placed to face up. Spectra were collected at a minimum of two different spots on the samples to verify the results.

Energy dispersive X-ray spectroscopy (EDS) was used to analyze the elemental composition on the wear surfaces, with a 3.5 kV acceleration voltage. To obtain the average elemental composition on the wear surfaces of the composites and the counterpart balls, at least three scans were executed with the size of the scanning areas about 465 × 350 μm². When studying the tribo-layer formed on the worn SiO₂ particles, at least 6 scans with small scanning areas ($\sim 8 \times 6 \mu\text{m}^2$) on the worn SiO₂ particles were performed.

3. Results and discussion

3.1. Influence of water lubrication

3.1.1. In water lubrication

Epomet-PTFE12.5 was tested via sliding against the Al₂O₃ ball, in water-lubricated conditions (boundary lubrication). The CoF decreases in the first 240 m sliding (reaching 0.068), followed by a significant increase of CoF to 0.165 after 500 m sliding. It is observed that in 7 tests, the measured sliding distance at which the CoF starts an increasing trend are 80, 100, 170, 200, 240, 430, 690 m, and the increasing slopes are also not the same. The case of 240 m is shown in Fig. 1b and the role of water and PTFE concentration on friction is shown in Fig. 1c. It is seen that both in water-lubricated conditions and dry sliding, a higher PTFE concentration in the composite leads to a lower CoF. In most cases, except sliding against the Epomet-PTFE12.5 for more than 300 m, water lubrication yields lower CoFs than dry sliding. This indicates that both PTFE and water molecules play an important role in lubrication at the sliding interface.

It is noteworthy that the wear rate of the composite Epomet-PTFE12.5 increases about 5.5 times in water-lubricated conditions (after CoF reaching 0.16), compared with $9 \pm 1.5 \times 10^{-16}$ m³/Nm in dry conditions. The corresponding wear rate of the Al₂O₃ ball also significantly increases by more than 20 times, reaching $3 \pm 1.6 \times 10^{-16}$ m³/Nm in water-lubricated conditions.

EDS analysis (3.5 kV acceleration voltage) detects around 2.4 ± 0.8 at.% Al on the worn SiO₂ particles after 100 m sliding, which means that a large amount of Al₂O₃ is transferred onto the wear surface of the composite in water-lubricated conditions. It should also be mentioned that 1.8 ± 0.5 at.% F was measured on the worn SiO₂ particles after 100 m sliding in water-lubricated conditions, much higher than the average F content (0.4 ± 0.1 at.%) measured outside the wear track of the composite. This implies the

Fig. 1. CoF curves of (a) the Epomet-PTFE12.5 under dry sliding condition and under water lubricated condition; (b) the Epomet-PTFE composites with different PTFE contents (12.5 wt.%, 2 wt.% and 0 wt.%) under dry sliding (35% RH) and distilled water lubrication (dotted curves), sliding against Al_2O_3 ball at 60 N and 2 cm/s velocity. The load used on 12.5 wt.% and 2 wt.% samples is 60 N, while the load used on 0 wt.% sample is 30 N to avoid triggering the stop condition of exceeding the maximum tangential force of the tribometer.

formation of a thin PTFE-containing tribo-layer on the wear surface of the composite in water-lubricated conditions. It should be noted that in dry sliding conditions, we measured about $1.4 \pm 0.4 \text{ at.}\%$ F and hardly any Al on the worn SiO_2 particles after 100 m sliding. To investigate the influence of water on the formation of PTFE transfer film and Al–F bonds, XPS analyses were performed on the wear surface of Al_2O_3 balls after sliding against the Epomet-PTFE12.5 for 100 m under dry sliding and in water-lubricated conditions, respectively. Measured $F 1s$ XPS spectra are shown in Fig. 2. Two evident F peaks at around 689.0 eV and around 685.3 eV are seen on the worn Al_2O_3 surface under dry sliding, whilst hardly any peak is observed on the worn Al_2O_3 surface sliding in water-lubricated conditions. The 685.3 eV peak points at the existence of metal–F bonds, while the peak at 689.0 eV is assigned to C–F bonds in PTFE [3,19,20]. The detected 689.0 eV peak suggests the existence of PTFE transfer films on Al_2O_3 ball surface, while the detected 685.3 eV peak indicates the formation of Al–F bonds on Al_2O_3 ball surface. Gao proposed a possible mechanism, assuming that radical reactions may occur between PTFE and metal during sliding, forming of metal–F bonds [5]. The missing of both the 689.0 eV peak and the 685.3 eV peak in water lubricated conditions means that there are no (or no detectable amount of) PTFE transfer films and Al–F bonds on Al_2O_3 ball surface. The XPS results indicate that when sliding in water-lubricated conditions, a water layer in the sliding interface

Fig. 2. XPS spectra of the wear scars of the Al_2O_3 ball after sliding for 100 m against the Epomet-PTFE12.5 under 35% RH dry sliding (top curve) and in water-lubricated conditions (bottom curve), at 60 N and 2 cm/s velocity. 30 scans were taken in both cases.

inhibits the formation of both PTFE transfer films and Al–F bonds on the worn Al_2O_3 surface.

In water-lubricated conditions, the significant increase of CoF after 300 m sliding against the Epomet-PTFE12.5 suggests a detrimental role of water on the PTFE lubrication when the test proceeds. The significant increase of the CoF and the wear rates of the composite and the Al_2O_3 ball indicates a partial loss of PTFE lubrication and poor water lubrication due to its low viscosity [21]. EDS results indicate the formation of a thin PTFE-containing tribo-layer on the worn composite surface, which could offer certain PTFE lubrication. XPS results reveal that the formation of both PTFE transfer films and Al–F bonds on the worn Al_2O_3 surface is inhibited in water-lubricated conditions. Therefore, the remaining PTFE lubrication is mainly from the PTFE-containing tribo-layer on the wear surface of the composite, within which PTFE lamellae could still slide over each other and reduce friction. The low CoF in the first 300 m is due to the combination of water lubrication and lubrication from the PTFE-containing tribo-layer on the wear surface of the composite. Hence, it is considered that in water-lubricated conditions, PTFE transfer films (if any) do not adhere strong enough on the ball surface and become unstable with water flow.

Fig. 3. CoF curves of the Epomet-PTFE12.5 sliding against the HF treated Al_2O_3 ball and the untreated Al_2O_3 ball in distilled water-lubricated conditions, at 60 N and 2 cm/s velocity.

Fig. 4. Schematic illustrations of a steel ball sliding over (a) a SiO_2 -epoxy composite without PTFE in dry conditions; (b) a PTFE- SiO_2 -epoxy composite in dry conditions; (c) a PTFE- SiO_2 -epoxy composite in water-lubricated conditions, without metal-F bonds; (d) a PTFE- SiO_2 -epoxy composite in water-lubricated conditions, with metal-F bonds. The relative scale bars have the same length in all figures, showing the different gaps (between the ball and the composite surfaces) in different cases.

Moreover, due to the lack of PTFE transfer film and Al-F bonds on the Al_2O_3 ball surface, the ball surface suffers from a severe wear due to the abrasion of SiO_2 particles that are only partly covered (or not covered) with the PTFE-containing tribo-layer. The roughness (R_a) of the worn Al_2O_3 surface increases from initially about 54 nm to about 156 nm (measured with confocal microscopy) when CoF reaches 0.13, while it only increases to around 85 nm when sliding under dry condition for 1000 m. After the CoF reaches 0.13, EDS results show an increase of Si content by about 2.5 at.% and a content of Al around 4 at.% (in dry sliding for 1000 m, Al is around 0.6 at.%) on the wear surface of the composite, comparing with the as-polished surface. Eventually, roughening of Al_2O_3 surface and accumulation of fractured SiO_2 particles and back-transferred Al_2O_3 on the wear surface of the composite give rise to a significant increase of CoF. The accumulation of fractured SiO_2 particles on the wear surface of the composite is also confirmed with light microscopy (not shown here). After the deterioration of the sliding surfaces ($\text{CoF} \approx 0.13$), it is found that when changing the sliding condition from water lubrication to dry sliding, the CoF immediately increases by about 0.015 and it keeps increasing upon further sliding.

3.1.2. Hydrofluoric-acid treatment

The inhibition of the formation of PTFE transfer films has been reported in water-lubricated conditions [9–11], but the inhibition of metal-F formation has not been reported by other authors.

A positive role of metal-F formation on the tribo-performance of the Al_2O_3 ball was found in our previous work [6]. It was shown that in comparison with an untreated Al_2O_3 ball, an F-terminated Al_2O_3 ball could reduce the friction when sliding against an F-terminated counterpart, e.g. a F-terminated steel disk or PTFE-lubricated composites. However, fluoridation of the Al_2O_3 ball alone could not reduce the friction when the sliding counterpart is not F-terminated. The reduction mechanism of friction can be attributed to a chemical passivation and a large repulsive force between two F-terminated surfaces [6].

In this study, a thin PTFE-containing tribo-layer was observed to form on the wear surface of the composite in water-lubricated conditions, but PTFE transfer films and Al-F bonds could not be formed on the worn Al_2O_3 surface due to the inhibition of the water boundary layer. As a consequence the single F-terminated wear surface of the composite in this case could not reduce the friction and wear on the Al_2O_3 surface, which is the main reason for its poor performance in water-lubricated conditions.

To verify this hypothesis, a hydrofluoric-acid treated Al_2O_3 ball (F-terminated) was tested against the Epomet-PTFE12.5 in water-lubricated conditions. EDS results show a content of F around 0.8 wt.% on the treated Al_2O_3 surface, indicating the formation of some Al-F compound on the surface. It is found that F elements are mainly decorating the grain boundaries (grain size: 2–15 μm), part of which are present in the grain boundaries at a depth up to

Fig. 5. CoF results of the Epomet-PTFE12.5 sliding against the steel ball under different loads for 1000 m, at 2 cm/s velocity and 35% RH.

about 10 μm from the surface. The friction result is shown in Fig. 3. Distinct from the untreated Al_2O_3 ball, the CoF (around 0.092) of the treated Al_2O_3 ball is fairly low and stable even after sliding for 1000 m. The wear rate of the treated Al_2O_3 ball (average wear depth around 3.8 μm after 1000 m sliding) is about one order of magnitude lower than that of the untreated Al_2O_3 ball (measured when CoF reaching 0.13 in the latter case) in water-lubricated conditions. This is attributed to the fact that the treated Al_2O_3 ball has also a (partly) F-terminated surface, resulting in sliding between the F-terminated Al_2O_3 surface and the thin PTFE-containing tribo-layer. It is noteworthy that the surface fluoridation of Al_2O_3 counterpart ball leads to a lower friction and improves its wear resistance in water-lubricated conditions. However, the wear rate of the treated Al_2O_3 ball is still higher than that of the untreated Al_2O_3 ball tested under dry sliding. due to the side effect of hydrofluoric-acid etching as well as water inhibiting the formation of PTFE transfer films. This result confirms the positive role of metal–F bonds formation on the tribo-performance of the Al_2O_3 ball when sliding against the PTFE based composites in water-lubricated conditions.

To summarize: in water-lubricated conditions, the water layer in the sliding interface inhibits the formation of PTFE transfer films and Al–F bonds, which results in a bad tribo-performance of the untreated Al_2O_3 ball. A pre-treatment of the Al_2O_3 with hydrofluoric acid creates a kind of Al–F compound and enhances considerably its tribo-performance in water-lubricated sliding. A schematic illustration of the effect of the repulsive force between two F-terminated surfaces and the effect of boundary water lubrication on a sliding contact is shown in Fig. 4. The formation of Al–F bonds could help to reduce the friction in the case of having no PTFE transfer film or PTFE transfer films only partly cover the wear scar of the ball.

3.2. Influence of normal load

The friction results of the Epomet-PTFE12.5 sliding against the steel ball under different normal loads (dry sliding) are shown in Fig. 5. A general trend is an increase of CoF with decreasing normal load. Moreover, there is a drastic increase of the CoF upon lowering the normal load from 10 N to 5 N, in comparison with the less sharply changed CoF values measured under high loads (10, 30 and 60 N). Especially at the onset of sliding test (within the first 200 m), the CoF values show a significant increase under low loads (0.5, 2 and 5 N), which double their initial CoF values by a nearly linear increase with sliding distance before reaching steady-state values. The amplitude of the increase of the CoF is inversely proportional to the normal load. It is clear that the load plays an important role in

Fig. 6. Light microscopy images of the worn surface of the Epomet-PTFE12.5 sliding against the steel ball for 1000 m under (a) 2 N, (b) 10 N and (c) 60 N load, at 2 cm/s velocity and 35% RH.

the friction behavior of the PTFE-filled composite. Light microscopy images of the worn surfaces of the Epomet-PTFE12.5 composite are presented in Fig. 6. An interesting finding is that under 2 N load, the worn surface of the composite shows many parallel scratches, whilst the worn surface under 60 N load is fairly smooth (confirmed with confocal microscopy). It is reasonable to correlate the high CoF under 2 N load to the parallel scratches and the rough surface. A transition is seen on the worn surface formed under 10 N load. The

Fig. 7. XPS F 1s core level spectra (20 scans) of the wear surface of steels after sliding for 100 m against the Epomet-PTFE12.5 under different loads, at 2 cm/s velocity and 35% RH. The inset graph shows a magnified portion of the main graph between 682.5 and 687.5 eV. The size of elliptical wear scars are presented in the legend (short side length $\times$ long side length).

wear track exhibits a smooth surface in the middle but a lot of parallel scratches near the two edges, which is due to the higher contact pressure in the middle than that near the edges in the ball-on-disc contact.

There are two possible reasons for this phenomenon: first, insufficient metal–F bonds are formed on the steel surface under low loads (<5 N) [22]; second, the contact pressures at low normal loads (<5 N) are too low to deform the composite and smear the PTFE into the sliding interface (on the epoxy and the SiO₂ surfaces as well as on the steel surface).

To test these two hypotheses, XPS measurements were carried out on the wear scars of the steel ball after sliding against the Epomet-PTFE12.5 for 100 m at various loads. The results are shown in Fig. 7. As aforementioned the peak at 685.2 ± 0.2 eV is due to the formation of Fe–F bonds, while the peak at 689.8 ± 0.2 eV is assigned to the C–F bonds of PTFE. It is seen that the area of the peak at around 689.8 ± 0.2 eV decreases with decreasing the normal load. This indicates that the amount of PTFE transfer films decreases with decreasing load. Therefore, the higher CoF values measured under lower normal loads could be, at least partly, due to the less amount of PTFE transfer film formed on the steel ball. As to the Fe–F bonds, it is found that the intensity of the corresponding peak are quite similar at all loading conditions, although under 60 N it is a bit higher which is probably due to its largest wear scar. The size of several wear scars are shown in the legend of Fig. 7. However, it is still very difficult to interpret the amount of Fe–F bonds in each case, because not only the size of wear scars, but also the thickness of PTFE transfer films above the Fe–F bonds affects the amount of measured Fe–F bonds with XPS. When there are some thick PTFE transfer films (>10 nm), Fe–F bonds beneath them cannot be detected. As shown in the figure, the left peaks of 5 N, 20 N and 60 N all have a slight shift to a higher binding energy than those of 0.1 N and 0.5 N, which is probably an indication of thicker PTFE transfer films (charging effect of PTFE). With thinner PTFE transfer films (0.5 N and 0.1 N), the possibility of Fe–F bonds being detected is higher. Nevertheless, the difference in the amounts of Fe–F bonds is not comparable with the difference in the amounts of PTFE transfer films. The different amounts of PTFE transfer films on the wear surface of steel balls is considered as the main reason for the different frictional behaviors. However, we cannot rule out the possibility that a higher load could soften the PTFE so that the limited shear strength of the material is decreased, which can also contribute to a decrease of CoF.

Fig. 8. EDS quantitative results of the F weight percentage on the original surface of the Epomet-PTFE12.5, as well as on its wear surface of the composite and worn SiO₂ particles surface, after sliding for 20 m against the steel ball under different loads, at 2 cm/s velocity and 35% RH.

Fig. 9. CoF results of the Epomet-PTFE12.5 sliding against the steel ball under 2 N load for 20 m, and changing load to 60 N for 20 m, and changing back to 2 N for 160 m. The test is performed at 2 cm/s velocity and 35% RH. The dash curve shows the result of a constant 2 N load test under the same sliding condition.

To verify further the second hypothesis, EDS analyses were done on the wear surface of the composite after sliding for 20 m against the steel ball at 0.5 N, 5 N and 60 N load. In all the cases, the content of F on the wear surface of the composite is always higher than on the as-polished composite surface. The value of F at.% on the wear surface of the composite increases with increasing normal load, as shown in Fig. 8. A similar trend of F at.% is also found on the worn SiO₂ surfaces. As aforementioned, the amount of PTFE transfer film also increases with increasing normal load, according to the XPS results. It indicates that sliding under a high load is beneficial to smearing PTFE over the SiO₂ and epoxy surfaces and onto the steel surface. This is attributed to a larger deformation of the composite under a higher load, which facilitates the squeezing out of the PTFE from the outer surface of the composite disc.

As a consequence under various loads, the determining factor of the CoF is the amount of PTFE in the sliding interface, while the influence of the amount of Fe–F bonds on the steel surface is not the predominant factor. To double check the hypothesis, a tribo-test of switching normal load 2 N–60 N–2 N was carried out. As shown in Fig. 9, it is observed that the CoF under 60 N load sharply decreases to 0.106 from 0.162 under 2 N load, and increases to 0.125 again as the normal load is changed back to 2 N. Besides, the increase of

Table 1

The measured apparent contact pressure, and whether or not Fe–F bonds are detected after 100 m sliding according to XPS results.

	Load applied on balls				Load applied on (near flat) spherical segment				
	60 N	5 N	0.5 N	0.1 N	0.5 N (1#)	0.5 N (2#)	1 N (1#)	1 N (2#)	2 N
Apparent pressure (MPa)	140 ± 8	45.2 ± 3	15.6 ± 1	7.9 ± 0.8	2.9 ± 0.4	4.1 ± 0.4	4.0 ± 0.3	6.2 ± 0.5	9.7 ± 0.6
Detection of Fe–F bonds (Yes or No)	Y	Y	Y	Y	N	N	N	Y	Y
Detection of PTFE (Yes or No)	Y	Y	Y	Y	Y	Y	Y	Y	Y

Fig. 10. XPS F 1s core level spectra (20 scans) of the wear scars of the polished steel (near flat) spherical segments after sliding for 100 m against the Epomet-PTFE12.5 under different low loads, at 2 cm/s velocity and 35% RH. The apparent contact pressure under 0.5 N is about 4.1 ± 0.4 MPa and under 1 N is about 6.2 ± 0.5 MPa. The dash curve of 0.1 N is adopted from Fig. 6.

CoF is slower after the normal load is switched back to the same load. This result demonstrates that more PTFE are smeared onto the wear surface of the composite under a higher load leading to an enhanced self-lubrication. Nevertheless, with further sliding under a low load (2 N), the amount of lubricating PTFE that was smeared into the sliding interface under a high load gradually reduces, and thus the CoF increases again.

It can be concluded that the normal load plays a crucial role in the friction behavior of the Epomet-PTFE composites. In contrast, the formation of Fe–F bonds is not significantly affected by the normal load. The amount of lubricating PTFE in the sliding interfaces under various loading conditions is the determining factor of the CoF values. A higher load facilitates the smearing of PTFE onto the wear surface of the composite as well as the transfer of PTFE onto the steel surface. With sufficient PTFE transfer films, the Fe–F bonds layer is beneath and mostly covered by the PTFE transfer films, which weakens its role in friction reduction.

Under a load as low as 0.1 N, we could still detect the formation of Fe–F bonds on the steel surface with XPS. Uçar et al. found that the minimum apparent contact pressure required to transfer PTFE onto the silicon oxide surface was less than 5 kPa at room temperature [23]. Thus, it is interesting to know if there is a minimum apparent contact pressure required to form Fe–F bonds. To increase the contact area and lower the contact pressure in tribo-tests, the $\phi 13$ mm steel ball was ground and polished until a spherical segment with a diameter of around 1 mm was polished off. The remaining surface of the spherical segment is not flat, but has a radius of curvature between 30 and 45 mm, with a roughness (Ra) around 60 nm.

As shown in Fig. 10, it is clear that when the contact pressure is reduced to a certain point, the peak at around 685.2 eV disappears or is immersed in noise, while the peak belonging to C–F bonds of PTFE is still observed. Thus, a minimum apparent contact pressure is required to form a detectable amount of Fe–F bonds under a sliding contact at room temperature. One possible explanation for the

formation of Fe–F bonds is probably that under a sufficient contact pressure, wear process regenerates fresh and highly reactive metallic Fe atoms from beneath the surface oxide layer [24], which could react with PTFE under forced contact. Korobov et al. [25] and Yorkov et al. [26] found that Fe-containing or Co-containing nanoparticles decomposed from precursors at around 280 °C in an argon atmosphere could react with PTFE nanoparticles (without external loading), forming a thin FeF_2 or CoF_2 interface layer between the two different particles. Tasker et al. [27], Ding et al. [28] and Cadman et al. [24] observed the formation of metal fluoride from the reaction between PTFE/Teflon AF and various metal vapors (Na, Al, Sn, In, Pb, Cd and Ni).

The effect of the apparent contact pressure on the formation of Fe–F bonds is summarized in Table 1. The apparent contact pressure was recorded, based on the measured apparent contact area on the steel surface after every tribo-test of 100 m. It is found that hardly any Fe–F bonds could be detected with XPS when the apparent contact pressure is below about 4 MPa. Under such a low pressure and resultant shear stress, it is unlikely to break the C–F bonds in the PTFE polymer chain. Onodera et al. found a bond dissociation reaction between carbon and fluorine atoms in the vicinity of an exposing aluminum atom in their quantum chemical molecular dynamics simulation method [22]. They inferred that the aluminum surface acted as a catalytic Lewis acid in which the fluorine atom was removed from the PTFE polymer chain. A similar mechanism may apply to the case of PTFE/steel sliding contact.

4. Conclusion

Effects of water lubrication and normal load on the formation of PTFE transfer films and metal–F bonds are investigated. It is found that different sliding conditions affect the formation of PTFE transfer films and formation of metal–F bonds on the wear surface of Al_2O_3 and 100Cr6 steel counterparts, which leads to different friction and wear performance.

Regarding sliding tests in water boundary lubrication, XPS analyses reveal that a continuous and flowing water layer in the sliding interface inhibits the formation of PTFE transfer films and Al–F bonds, resulting in a detrimental effect of liquid water on tribo-performance. A hydrofluoric-acid treatment of the Al_2O_3 ball enhances considerably its tribo-performance in water-lubricated sliding, which demonstrates the important role of Al–F formation in water-lubricated sliding.

Under various loading conditions, an increase in CoF with decreasing load is observed. The main reason, based on EDS and XPS analysis, is that a higher load facilitates smearing of PTFE onto the wear surface of the Epomet-PTFE composite and the transfer of PTFE onto the steel surface. The formation of Fe–F bonds does not evidently affect the tribo-performance when sliding under different loads. During sliding, there is a minimum apparent contact pressure required to form a detectable amount (via XPS) of Fe–F bonds on the wear surface of steel.

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