Molecule Structure Variations in Friction of Stainless Steel / PTFE and Its Composite

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Synopsis

The friction and wear characteristics of PTFE and one of its composites, JS material rubbing against stainless steel, were determined with a pin-disk tester in this study. The JS material is a multilayer composite composed of PTFE layer containing metal oxide and others, porous bronze layer, copper-plating layer and steel back. The submicroscopic features of frictional surfaces of stainless steel and JS materials were observed with an electron probe microanalyzer (EPM). By analysis of frictional surfaces of stainless steel pins in various operating stages with X-ray photoelectron spectroscopy (XPS), chemical shifts of C_{1s}, O_{1s}, and F_{1s} peaks, F-ion gathering in surface transfer films, and generation of a metal fluoride and an unknown compound containing oxygen were found. The determination of JS material wear debris with electron spin resonance spectroscopy (ESR) showed that polymeric radicals different in structure and stable in air existed. The authors consider that these PTFE molecule structure variations might be of benefit to the adhesion of PTFE transfer film to the rubbed stainless steel surface, which is important to improve the friction and wear performance of PTFE.

INTRODUCTION

The smooth surface and column form structure of the PTFE molecule enable it to have lower surface energy. PTFE molecules easily slip over each other. The bonded crystals are easily drawn out, and transfer onto the mating surface, forming an oriented thin film which results in low friction and high wear of PTFE.[1,2] However, a lot of recent research indicates that far more complicated changes occurred at the frictional interface by PTFE and its composites rubbing against metals. One of the interesting subjects is the tribochemical effect, which is concerned with the PTFE molecule structure, aggregational state, its interaction with mating rubbing metals, atmospheric substances, and so on. For example, Brainard and Buckley[3] studied the adhesion of PTFE to a clean surface of tungsten with a field ion microscope and found a very strong carbon—metal bond at the polymer–metal interface, leading to a breakage of the C—C covalent bond in polymer. They suggested that a chemical bond was generated between PTFE and the clean metal in the transfer of PTFE onto the metal surface. Friction experiments of PTFE against stainless steel or other metal have been conducted with various methods by Wheeler,[4] Cadman and Gossedge,[5] and the authors,[6] respectively. The friction tracks of metal surfaces were examined with XPS, finding the existence of F-ions. This indicates that C—F bond rupture occurred in PTFE molecules during rubbing, and the F-ions reacted further with metal oxides or metal.
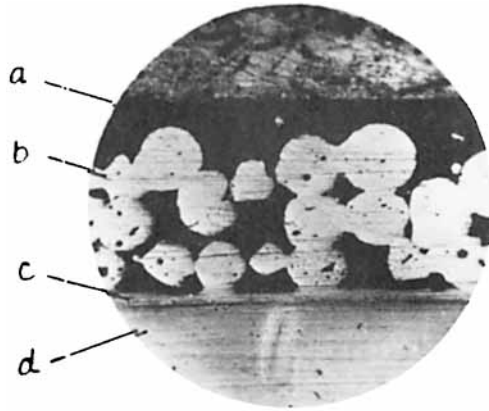
Fig. 1. The microphotograph of cross-sectional profile of JS material (100×): (a) surface plastic layer; (b) porous bronzy layer; (c) copper-plating layer; (d) steel back.

Richardson and Pascoe[7] studied the catalytical effect of clean surface of iron film on the decomposition of n-C5F12, a simulated substance of PTFE, and found that n-C5F12 was ruptured into molecule fragments: CF3+, C2F5+, C3F7+, etc. The study of the molecule characteristics of PTFE wear debris by Hu and Eiss[8] also suggested that the pulling out of PTFE materials coupled with a fracture and/or slippage of molecular chains and the molecular weight of debris was 1–2 orders of magnitude lower than that of the bulk samples. These tribochemical effects changed the structure and the aggregational state of PTFE molecule, but it seems to be a tendentious view of many researchers that they are of advantage in improving the antifriction performance of PTFE composites. However, it should be noted that many problems on the tribochemistry of PTFE/metal are still unclear and remain to be investigated by the researchers in the tribological field. In this aspect, the authors thought that it was very important to clarify the following three fundamental problems: (1) the mechanism and the causes of chemical reaction at the rubbing interface of PTFE/metal; (2) the relationship between the tribochemical effects and adhesive characteristics of PTFE transfer film; (3) the influence of the variation of molecule structure and molecule state of PTFE on its friction and wear performance.

The purpose of this study is to explore some tribochemical effects, the structure variations of PTFE molecule, and their relationship with the friction and wear performance of pure PTFE and JS material in friction of stainless steel/PTFE and JS material.

EXPERIMENTS

Test Materials

The materials used in this study are: pure PTFE made in Jinan Chemical Factory, China, JS material made in our Institute and home-made stainless steel (1Cr18Ni9Ti). Pure PTFE and JS material were separately lathed to

D50 × 10 mm and D50 × 3 mm disks. Stainless steel was lathed to D5 × 25 mm pins. The pin drilled a D2 mm hole on its axis, the hole bottom is at distance of 1 mm from outer frictional surface, and a thermocouple was inserted into the hole in the test; then, the temperature rise of the hole bottom is approximately considered as temperature rise of the frictional surface.

Apparatus and Instruments

The friction and wear experiments were conducted with Xuanwu 3 pin-disk tester designed by our Institute. Analysis of the friction surfaces of pin and disk after rubbing were conducted with EPM-810 electron probe micro-analyzer made in Japan and PHI-550 ESCA/SAM system made by the Perkin-Elmer Corp. The wear debris of pure PTFE and JS material was tested with an E-115 electron paramagnetic resonance spectroscope made by the Varian Corp.

Test Procedure

Before friction tests the stainless steel pins were abraded with the alumina papers nos. 200, 500, 700, and 900 successively. The friction surfaces of pins and disks were carefully cleaned with distilled water and acetone separately.

Pure PTFE Rubbing against Stainless Steel. The friction and wear tests were carried out on a pin-disk tester, and the friction coefficient and surface temperature rise were determined. After the operation was stopped, the PTFE wear rate was detected by means of the loss in weight. Then, the analyses of friction surface of stainless steel pin with EPM and XPS and of PTFE wear debris with ESR were conducted.

JS Material Rubbing against Stainless Steel. The friction and wear tests were also conducted on the pin-disk tester until the material failed. At the ends of individual periods tests were stopped, pin and disk were removed, the wear rate of JS material disk was detected by means of loss in weight, and the EPM determination of pin and disk friction surfaces and the XPS determination of pin friction surfaces were carried out. Then, the pin and the disk were installed in pin-disk tester and put into operation again. The wear debris of JS material was collected periodically, and the ESR determination of the debris was conducted.

RESULTS AND DISCUSSION

Friction and Wear Characteristics of Pure PTFE, JS Material Rubbing against Stainless Steel

The friction and wear test results are listed in Table I. The EPM determination results of the pin and disk friction surfaces are shown in Figures 2–5.

It is seen from Table I that the mean wear rate of pure PTFE rubbing stainless steel is far larger than that of JS material, and the friction coefficient is about 1.5–2.0 times of that of JS material. The friction trace and PTFE transfer fragments on the friction surface of stainless steel are visible on the microphotograph of Figure 2.

Fig. 2. The microphotograph of friction surface of stainless steel rubbed against pure PTFE for 1 h (100×).

The data in Table I also illustrate that there is a good corresponding relationship between the friction coefficients and wear rate when JS material rubs against stainless steel. In accordance with the mean wear rate of JS material in frictional test (Table I) and atomic relative concentrations obtained from XPS determination of stainless steel friction surface (Table II), the whole operating period might be divided into three stages: The first is from friction start to end of the first hour, the second is from end of the first hour to end of the 88th hour, the third is from end of the 88th hour to end of the whole test.

The first is the run-in stage. In this stage the surface plastic layer of JS material was planed by the rough surface of steel pin with a high rate, and the completed transfer film on the mating surface of stainless steel had not yet formed.
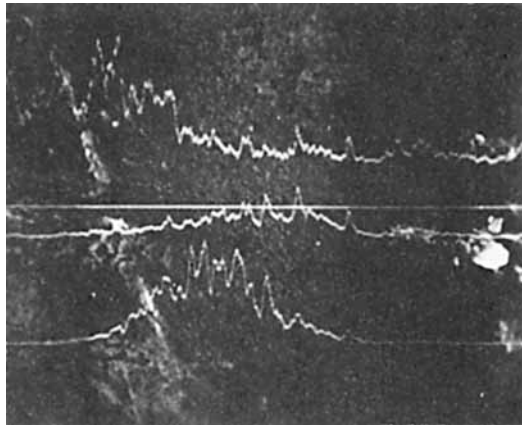

Fig. 3. The microphotograph of friction surface of stainless steel rubbed against JS material for 10 h (100×). The line represents scanning line of electron beam and the three curves represent the distributions of the elements F, Pb, and Cu, respectively, from top to bottom.
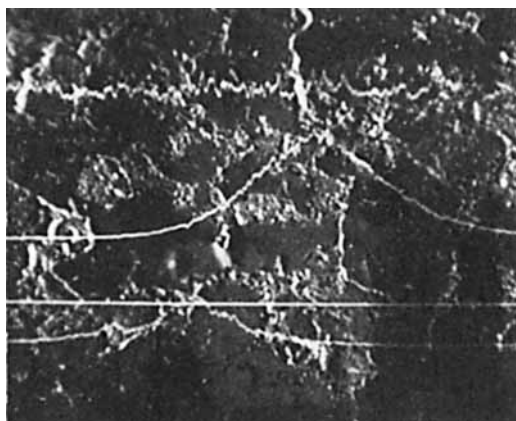
Fig. 4. The microphotograph of friction surface of JS material rubbing against stainless steel for 10 h (100×). The curves represent the distributions of elements: F, Pb, and Cu, respectively, from top to bottom.

At the second stage, the bronze sintered particles in the porous layer of JS material were gradually exposed on the friction surface, carrying the greater part of external load, and pressing the PTFE molecules onto the opposite frictional surface closely. In the meantime, the bronze surface was covered with a PTFE transfer film because of the converse transfer of PTFE. Hence, the fine and firm transfer films were formed on the steel pin surface and the bronze friction surface of JS material, which reduced the friction and the wear effectively. The transfer films could be removed locally, but the PTFE in the porous layer would be replenished immediately, and the transfer films formed again.

In the last stage, the porous bronze layer of JS material was worn thinner, the bronze area on the friction surface was enlarged, and the greater part of PTFE filling in the bronze pores was exhausted simultaneously. As the
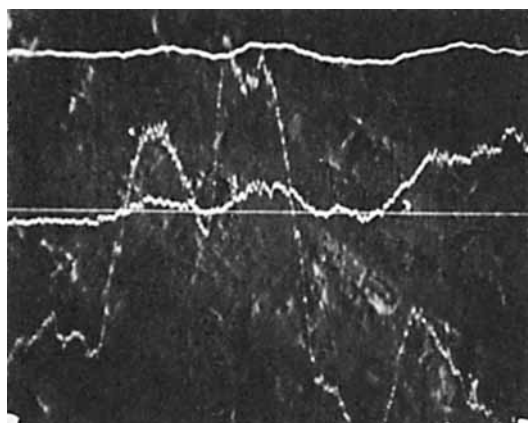

Fig. 5. The microphotograph of friction surface of stainless steel rubbed against JS material after which it failed (200×). The curves represent the distributions of elements: F, Pb, and Cu, respectively, from top to bottom.

TABLE I
Friction and Wear Test Results[a]

Frictional pairs	Operating time (h)	Mean wear rates of disk (g/h)	Frictional coefficients	Temperature rises due to friction (°C)
Stainless steel pin/ PTFE disk	1	0.0671	0.16–0.19	80–88
Stainless steel pin/ JS material disk	1/60	0.0024	0.08	~ 50
	1		0.08–0.09	55–83
	5	0.0023	0.07–0.09	80–105
	26	0.0018	0.08–0.09	89–105
	78	0.0006	0.08–0.10	89–117
	88	0.0027	0.08–0.11	75–120
	115	0.0060	0.08–0.15	70–125

[a] The test condition: load 3.92×10^6 Pa, revolution 1200 r/min (line speed 3.14 m/s), in air, at room temperature.

worn-out PTFE films on both the friction surfaces cannot be duly compensated, the uniform transfer films were destroyed, causing a direct rubbing of stainless steel against bronze; thus, the lubrication eventually failed. As seen from Figure 4, the "bronze island" is surrounded by filled PTFE on the JS material surface. The bronze surface is covered by a converse transfer layer of PTFE, and the three curves indicate the line distributions of the elements F, Cu and Pb. The stainless steel surface was also covered by a fine transfer film, and a frictional trace on it could be indistinctly seen as shown in Figure 3. Figure 5 shows the fluctuation of the Cu distribution on the steel surface due to the inhomogeneous transfer of bronze on the surface after the destruction of the PTFE transfer film.

TABLE II
The Binding Energies and the Atomic Concentrations of Main Elements on the Stainless Steel
Friction Surface Rubbing against JS Material at Various Operating Periods[a]

Operating time (h)	Binding energies (eV)								Atomic relative concentration (%)		
	F_{1s}		C_{1s}				O_{1s}		F	C	O
0					284.8	532.3	531.6	530.3	0	77.0	6.6
1/60	689.0	684.7	291.8	286.8	284.9	533.7		530.3	44.7	31.6	8.9
1	689.0	684.6	291.8	286.9	284.8	533.7	532.5	530.2	55.5	22.6	4.7
5	689.0	684.5	291.8	286.9	285.1	533.7	532.5	530.2	52.9	21.4	6.8
26	689.0	684.5	291.8	286.9	285.1	533.6	532.4	530.3	53.0	22.8	5.6
88	689.0	684.5	291.7	288.4	285.1	533.6	532.4	530.3	54.1	23.7	4.9
115	689.0	684.5	291.7		280.5	533.7	532.3	530.3	47.4	20.3	7.3

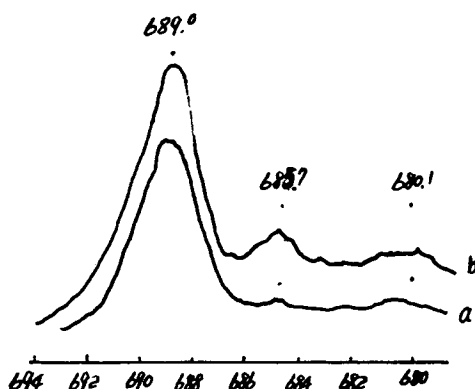[a] The friction test condition was same as that in Table I.

Fig. 6. F_{1s}–XPS spectra of stainless steel surfaces rubbed against pure PTFE and JS material: (a) the stainless steel surface rubbed against pure PTFE for 1 h; (b) the stainless steel surface rubbed against JS material for 1 h.

The Tribochemical Effects Obtained in XPS Analyses of Friction Surfaces of Stainless Steel

The results of XPS determination of stainless steel friction surfaces rubbed against pure PTFE and JS material are shown in Figures 6–8 and Table II.

The results in Figure 6 illustrate that when pure PTFE and JS material were rubbed against stainless steel, the transfer film on stainless steel friction surface contained not only a lot of PTFE (the binding energy of F_{1s} character-istic peak is 689.0 eV), but also metal fluoride with an F_{1s} peak of binding energy 684.6 eV. This value is identical to that of the F_{1s} for NiF_2, according to the *Handbook of X-Ray Photoelectron Spectroscopy*[9] published by Perkin-Elmer. However, the F_{1s} peak of metal fluoride on stainless steel surface rubbed against JS material is stronger than that on stainless steel surface rubbed against pure PTFE.
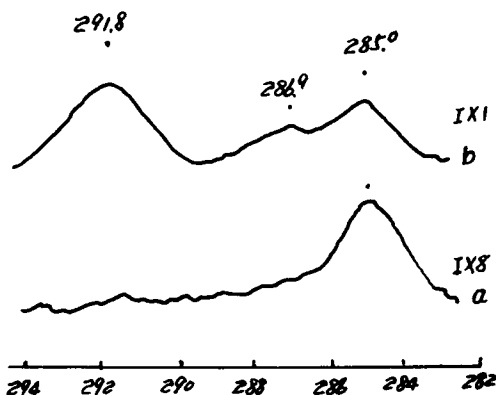

Fig. 7. C_{1s}–XPS spectra of stainless steel surface rubbed against JS material: (a) the stainless steel surface before friction; (b) the stainless steel surface rubbed against JS material for 1 h.

Fig. 8. O_{1s}–XPS spectra of stainless steel surface rubbed against JS material: (a) the stainless steel surface before friction; (b) the stainless steel surface rubbed against JS material for 1 h.
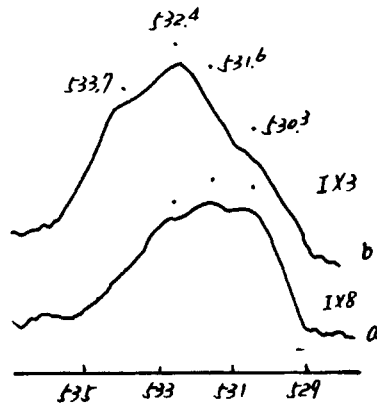
Figures 7 and 8 and Table II indicate that some complications appear in the O_{1s} and C_{1s} spectra on stainless steel surface rubbed against JS material. In Figure 7, the binding energy of C_{1s} peak in PTFE is 291.8 eV, and that of the C_{1s} peak in the surface contaminations is 285.0 eV. In addition, an unknown C_{1s} peak with a binding energy 286.9 eV is revealed.

It is well known that the composition of surface oxides for multicomponent alloy is complicated. It may be the mixture of oxide cocrystals, the compound of solid solution type, or the substance of chemical compound type. Therefore, there cannot be only a single peak in the O_{1s}–XPS spectrum. The curve a in Figure 7 indicates that there are at least three valences in the O_{1s} spectrum of oxides on stainless steel surface before rubbing and their binding energy are 530.3, 531.6, and 532.4 eV, respectively. After rubbing for 1 h, the stainless steel surface was covered by the transfer film, the O_{1s} peak of 532.4 eV increases, and an unknown O_{1s} peak of 533.7 eV is revealed. All these illustrate that unknown compounds containing oxygen were generated in the transfer film on steel pin surface.

The atomic relative concentrations of the main elements on the steel pin surface rubbed against JS material in various periods are listed in Table II. It is known from the table that, in the run-in stage, the transfer film cover on steel surface was not complete. In the last stage, the fluor atomic relative concentration was lower because the transfer film was destroyed. While in the stably operating middle stage, the fluor atomic relative concentration was higher because the surface was covered with a uniform fine transfer film. In addition, in the middle and last stages, a high F/C ratio of atomic relative concentrations, about 2.5, is maintained, which is larger than that of PTFE—2.0. This result is consistent with the above-mentioned formation of metal fluoride. All of these illustrate that the F-ion gathering occurred in the transfer film. In the primary stage the higher carbon atomic relative concentration is due to the incomplete cover of transfer film and partial contamination remaining on the steel surface. The oxygen atomic relative concentration was higher also because of the incomplete cover of the transfer film and the exposure of metal oxides on the surface.

Fig. 9.   ESR spectra of fragments and wear debris of pure PTFE: (a) PTFE fragments cut with a shive; (b) PTFE wear debris collected from pure PTFE rubbing against stainless steel for 1 h.
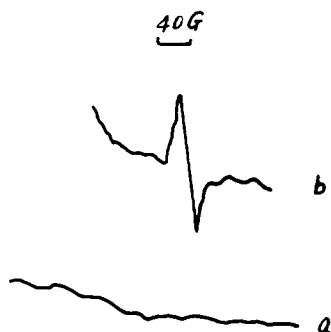

Fig. 10.   ESR spectra of fragment and wear debris of JS material: (a) the fragments cut from the surface plastic layer of material with a shive; (b) JS material wear debris collected from JS material rubbing against stainless steel for 1 h.

The ESR Determinations of Polymeric Radicals Resulted from Rubbing

The results of ESR determination of the wear debris generated from pure PTFE and JS material rubbing against stainless steel are shown in Figures 9–12.

It is proved by the ESR determinations of JS material wear debris that polymeric radicals were generated in the frictional processes of JS material/ stainless steel. Because of the various mechanisms of PTFE molecule fracture and radical reaction, polymeric radicals different in structure might be generated; therefore their ESR spectra are different, as seen as Figures 10 and 11.

Fig. 11.   The ESR spectrum of JS material wear debris collected from stainless steel/JS material rubbing for 2 h.
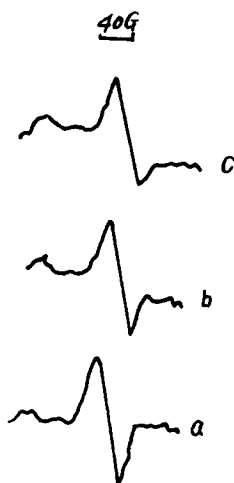
Fig. 12. The relationship between the time and peak strength of ESR spectrum of JS material wear debris kept in air, which were collected from stainless steel/JS material rubbing for 1 h: (a) kept in air for 14 min; (b) kept in air for 34 min; (c) kept in air for 1 h.

PTFE radicals resulting from mechanical reasons had been determined in certain ESR researches[10–12] formerly. They were usually radicals of fracture type, which react actively with environmental oxygen to form peroxide radical: $-CF_2-CFOO^*$.

In accordance with these results of the researches and ours, the authors consider that the spectrum in Figure 11 is probably that of PTFE peroxide radical. Under the friction test condition of the present research, the PTFE radicals just generated (or the peroxide radical generated by reaction with the oxygen in atmosphere) may be caught (or trapped) in the internal defects of PTFE crystal lattice, without being influenced by surrounding atmosphere, resulting in a longer life. As shown in Figure 12, after the test sample was kept in air at room temperature for 14 min, 34 min, and 1 h, no variations in its ESR spectrum were found. However, it should be noted that, under other test conditions, the radical might also exist on the crystal surface in air at room temperature, and it decays with time gradually. One of authors is now carrying on this work. Even though pure PTFE was used in rubbing against stainless steel, the paramagnetic characteristic of the PTFE wear debris also varied in an ESR magnetic field, as seen in Figure 9. But the ESR signal is too weak to judge the formation of radicals.

PTFE Molecule Structure Variations in the Frictional Processes

1. The PTFE molecule are subjected to mechanical compression, tension and shear to be deformed, slipped between their chain sections, even broken at the $-C-C-$ or $-C-F-$ bonds in the molecules.

2. Frictional heat makes interfacial temperature rise, and the temperature at local area (namely, heat point) might exceed that of the PTFE decomposition; therefore, thermal vibration of PTFE molecule chains is enhanced, resulting in the softening, melting, and even decompositing of the PTFE.

3. Because of static electricity and van der Waals forces, PTFE molecules are adhered onto the metal oxides or instantaneously existing fresh metal on
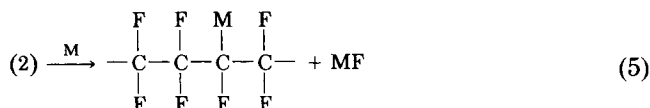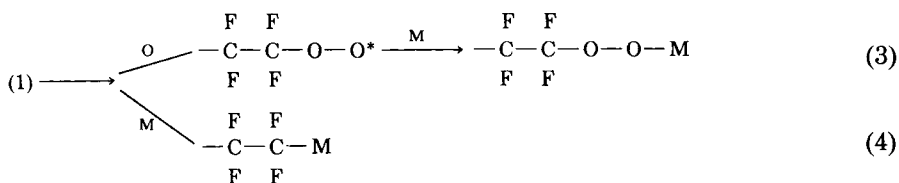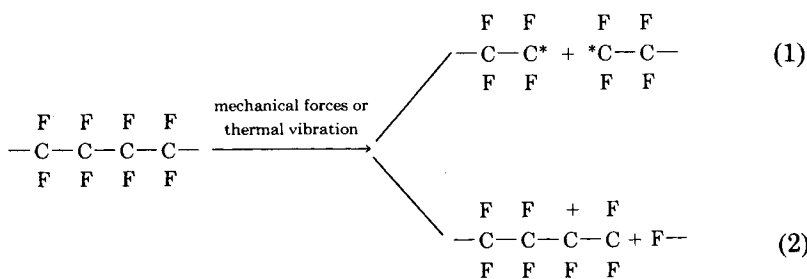
mating surface in the friction. For the same reasons, PTFE molecules can also be adhered onto the bronze surface of the JS material by PTFE converse transfer. Hence, semicrystal PTFE is changed to the directionally oriented transfer layer on metal surface.

4. Besides the above-mentioned points there are three factors which affect the PTFE molecule structure as follows:

a. The direct contacts between the bronze surface of JS material and stainless steel surface might lead to the removal of their surface oxides by friction. The fresh metal is exposed, which could catalyze the PTFE decomposition, if that contacts with the PTFE molecules. At the time, the fresh metal surface has the function of ejecting exoelectrons with low energy (about 1–4 eV). The exoelectrons make organic compounds decompose and can also excite other organic reaction.[13]

b. The oxides on mating metal surface, the oxides in composite, such as lead oxide, or other substances might exothermally react with PTFE on the interface.[14] In particular, the exothermal reaction is very severe when PTFE melts.

c. One of the characteristics of polymeric radicals of mechanical fracture type is that oxygen has a strong reactivity to them.[11] In the frictional test of the present study, the oxygen in air reacted with PTFE fracture radicals, forming peroxide radicals. According to the above-mentioned, we infer that PTFE molecule structure variations proceed as follows:

$$
\begin{array}{c}
\text{F \quad F \quad\quad F \quad F} \\
-\text{C}-\text{C}^* + {}^*\text{C}-\text{C}- \\
\text{F \quad F \quad\quad F \quad F}
\end{array}
\quad (1)
$$

$$
\begin{array}{ccc}
\text{F \quad F \quad F \quad F} \\
-\text{C}-\text{C}-\text{C}-\text{C}- \xrightarrow[\text{thermal vibration}]{\text{mechanical forces or}} \\
\text{F \quad F \quad F \quad F}
\end{array}
$$

$$
\begin{array}{c}
\text{F \quad F \quad + \quad F} \\
-\text{C}-\text{C}-\text{C}-\text{C} + \text{F}- \\
\text{F \quad F \quad F \quad F}
\end{array}
\quad (2)
$$

$$
(1) \longrightarrow
\begin{array}{c}
\text{O} \quad
\begin{array}{c}
\text{F \quad F} \\
-\text{C}-\text{C}-\text{O}-\text{O}^* \xrightarrow{\text{M}} \\
\text{F \quad F}
\end{array}
\quad
\begin{array}{c}
\text{F \quad F} \\
-\text{C}-\text{C}-\text{O}-\text{O}-\text{M} \\
\text{F \quad F}
\end{array}
\quad (3)
\end{array}
$$

$$
\begin{array}{c}
\text{M} \quad
\begin{array}{c}
\text{F \quad F} \\
-\text{C}-\text{C}-\text{M} \\
\text{F \quad F}
\end{array}
\quad (4)
\end{array}
$$

$$
(2) \xrightarrow{\text{M}}
\begin{array}{c}
\text{F \quad F \quad M \quad F} \\
-\text{C}-\text{C}-\text{C}-\text{C}- + \text{MF} \\
\text{F \quad F \quad F \quad F}
\end{array}
\quad (5)
$$

where M represents the metal atom or other electron giver atom.

Adhesive Characteristic of PTFE Transfer Film on Metal Surface

Beyond doubt, PTFE material may adhere to the metal surface due to mechanical embedment or static electric attraction when they rub against the metal. However, the emphasized problem is why PTFE transfer film adheres to the metal surface so strongly. It is obviously unsatisfactory to explain this phenomenon by mechanical embedment and static electric attraction mechanism only. The XPS and ESR determination results obtained in the present study demonstrate that when PTFE, especially PTFE composite, is rubbed against metal, mechanochemical, or thermal degradation of PTFE molecules takes place. The fracture of $-C-C-$ and $-C-F-$ bonds lead to the compound generations which are different from PTFE in structure and thus in characteristics. Besides the NiF_2, which can be identified by 684.6 eV peak of the F_{1s}–XPS spectra, there is a kind of organic fluorides whose XPS spectra of C_{1s} and O_{1s} is completely unknown.

In accordance with peroxide radical determined by ESR, the authors infer that an oxygen-containing organic fluoride is possibly formed in the frictional process. An oxygen-containing group, such as carbonyl, hydroxy, ethereous group, etc. is introduced into the PTFE molecule, and PTFE molecules are chemically adhered onto the metal surface due to their strong polarities It is also possible to form a new type of compound, which links with metal surface by ion bond or coordinative bond. When metal surface is damaged to form a new fresh surface, the valence of the metal atoms at fresh surface is unsaturated. The suspension bond in a higher energy state encounters the excited PTFE molecules (or PTFE radicals) and the reaction between them immediately occurs. The binding generations lower their energy level, but metal atoms still remain in the primary crystal lattice at that time. In short, the existence of chemical bonds between PTFE molecules and metal surface greatly enhances their adhesive strength to metal surface, making them remain on the metal surface for a longer time; hence the friction and wear are reduced.

In comparison with pure PTFE, the supporting role of porous bronze layer in JS material resulted in larger contact stress at the interface, which was beneficial to the generation of fresh metal surface and local heat point, the formation of fracture polymer radicals, and close transfer of PTFE to mating surface. The incorporated fillers, such as lead oxide, can exothermally react with PTFE. The react products might contain oxygen.[14] Thus the PTFE molecules are more strongly adhered to mating surface. It greatly reduced the PTFE wear.

CONCLUSION

1. Under the friction test conditions of present study, a uniform PTFE transfer film was formed on the stainless steel surface rubbed against pure PTFE and JS material, and was also formed on the bronze surface of JS material itself.

2. The XPS analysis of the transfer film on stainless steel friction surface indicates that chemical shifts of C_{1s}, O_{1s}, and F_{1s} peaks and F-ion gathering in the transfer film occurred. The analytical data also indicate that a metal fluoride (NiF_2) and unknown oxygen-containing compounds were formed on

stainless steel surfaces. The F_{1s} peak strength of metal fluoride on the stainless steel rubbed against JS material was larger than that rubbed against pure PTFE. This illustrates that JS material is more beneficial to the occurrence of tribochemical reaction than pure PTFE.

3. ESR determination of wear debris indicate that the molecular paramagnetic characteristics of all wear debris of pure PTFE and JS material were changed. The wear debris of JS material contains polymeric radicals different in structure. The radicals generated under the present test conditions were stable in air at room temperature, and their ESR peak strengths were able to remain unchanged for a longer time.

4. In the frictional test of the present study, PTFE molecules chemically reacted with the rubbed material, some substances in atmosphere, etc. The PTFE molecule structure on material surfaces was changed.

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