

Boundary Lubrication from the Viewpoint of Surface Chemistry
—Role of nascent surface on tribochemical reaction of lubricant additives—



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Chemical properties of nascent surfaces of tribo-materials were reviewed from the viewpoint of tribochemical activation. In general, material surfaces are covered with metal oxides and organic contaminants, and are chemically stabilized. Once the surface layers are removed mechanically, nascent surfaces are formed at mechanical contact. The chemical nature of the nascent surfaces of metals and ceramics was estimated by a method developed by the author. Chemisorption and surface reactions of model compounds of lubricant components on nascent surfaces were monitored during friction tests in vacuum by a quadrupole mass spectrometer. The chemical activity of nascent steel surfaces can be explained by Pearson's HSAB principle. The chemical nature of nascent aluminum surfaces was found to be different from that of nascent steel surfaces as a transition metal. Nascent ceramic surfaces exhibited such high activity that even hydrocarbons could chemisorb on them. It was found that synthetic-hydrocarbon base oil was decomposed during lubrication tests in a vacuum, and hydrogen and hydrocarbons with low molecular weight were evolved under the effects of the nascent steel surface and temperature rise at the contact. The role of the tribochemical process on boundary lubrication properties of lubricant additives is discussed by the chemisorption activity of nascent surfaces of metals and ceramics based on tribological performance of additives. For example, tribological behavior of extreme pressure additives under severe conditions can be explained by the chemisorption and reaction of EP additives on nascent steel surfaces. In conclusion, the surface chemistry of boundary lubrication is closely dependent on the contact condition.

Key Words: boundary lubrication, tribochemistry, nascent surface, adsorption, surface reaction, lubricant additive

1. Boundary Lubrication and Surface Chemistry

Tribological characteristics in boundary lubrication strongly depend on the mechanical properties of the boundary lubrication film at contact interface. The boundary lubrication film is an absorption film or reaction film on the material surface and is formed by reactions during friction. Consequently, chemical reactions at the contact interface must be understood to understand the boundary lubrication phenomena (Fig. 1). There are four factors for the reaction, (A) lubricant components, (B) material and (C) oxygen, water, etc. in the atmosphere are responsible. Further, (D) contact conditions such as load (contact pressure) and friction speed are important factors for reactions in the formation of boundary lubrication film. That is, for the boundary lubrication, not only lubricant components but also tribo-materials and environments as well as contact conditions are related

via the formation of a boundary lubrication film, and it is apparent that tribochemical reactions at the friction interface are deeply involved in the boundary lubrication.

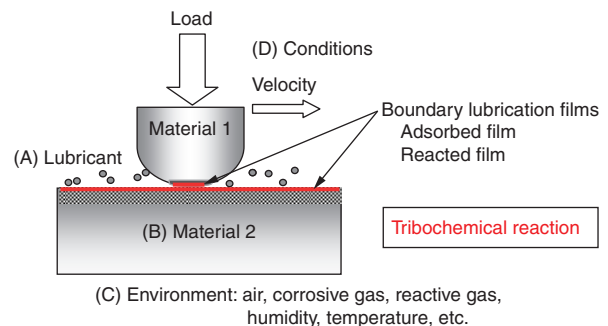


Fig. 1 Four factors for boundary film formation by tribochemical reactions

2. Mysterious Phenomena

We call chemical phenomena in tribology as tribochemistry. On the other hand, researchers who handle fine particles call chemical phenomena in pulverization as mechanochemistry. Heinicke, who did pioneering work in this field, used the word "Tribochemie", that is, tribochemistry, in his book¹⁾ in the meaning of chemical phenomena in which dynamic (mechanical) energy is involved, mechanochemistry is considered to be appropriate. In this book, Heinicke cited many examples of mechanochemical reactions in a large number of reactions such as syntheses and decompositions of organic materials and inorganic materials, indicating that activation by dynamic action is possible for chemical phenomena in general.

When we are reading papers on tribology, the word of tribochemical reaction is found when authors come across mysterious phenomena. When abnormal friction and wear data is obtained but is unable to be explained by conventional common knowledge, the unknown facts may be attributed to tribochemistry, such as "tribochemical reactions occurred" or "seems to be caused by tribochemical reactions," etc. For example, Professor Fischer at Stevens Institute of Technology, who is a friend of mine of 20 years' standing, explained that tribochemical reactions took place on the friction surface because the hydrocarbon liquid having no functional group lowered the friction coefficient of ceramics²⁾. In this regard, however, he did not analyze reaction products and did not confirm tribochemical reactions at that time.

Because chemical reactions are "changing phenomena," physical properties of products formed by chemical reactions are considerably changed. Hard diamond changes to carbon dioxide in oxidation reaction and a product which has completely dissimilar properties is formed. Litmus paper turns red under acidic conditions and turns blue under basic conditions. Because the phenomena occurred by chemical reaction are nonlinear in this way, it is difficult to predict the phenomena. The ancestor of modern chemistry is alchemy. In chemistry, there are some points which do not seem mysterious even if anything mysterious occurs, and the word of tribochemistry is sometimes used like mystery or miracle. However, tribochemistry is also a natural phenomenon, which occurs based on chemical principles, and certainly would be able to be logically explained and technically controlled.

3. Chemical Reactions and Energy

The concept of chemistry is able to be roughly classified into two broad categories³⁾. One is a microscopic view in which natural phenomena are tried to be understood on

the basis of molecular structure. Understanding of natural phenomena on the basis of molecular structure including the progress of nanotechnology and computational science structure has been proceeding in recent years, and we are now in the age in which even a molecular design is enabled. The other is a macroscopic view in which natural phenomena are tried to be understood by temperature, pressure and concentration, etc. Thermodynamics is this, and is a view to understand natural phenomena by the macroscopic parameters mentioned above. A thermal engine, a plant's thermal balance and thermochemical reactions are all technologies or natural phenomena involving thermal energy, and the change is observed when Gibbs free energy ΔG is negative. Even for thermochemical reactions, results by the reactions can be predicted when the reactions are observed in beakers under given conditions of temperature, pressure and concentrations, etc. For example, the oxidation reaction can be regarded as a phenomenon in which the chemical energy of compounds is liberated by the reaction.

Since mechanical energy other than heat is involved, it is difficult to predict tribochemical reactions. Water is formed by the thermal reaction of hydrogen and oxygen. The reverse reaction does not occur at room temperature because ΔG is positive. However, water is decomposed into hydrogen and oxygen by the electrolysis of water even at room temperature, because electric energy is involved in this. On the other hand, combustion (oxidation) of sugar can produce water, carbon dioxide, and reaction heat. Against this, photosynthesis is the reverse reaction to produce sugar and oxygen from water and carbon dioxide, and this does not occur at room temperature but is enabled by optical energy.

A tribochemical reaction is a chemical reaction in which mechanical energy is involved. Energy has a quality, and the quality of mechanical energy is higher than that of electric, optical, chemical and thermal energies (Fig. 2). High-quality mechanical energy is easily converted to other energies. For example, when metal is ground by a grinder, we can easily realize that the mechanical energy is converted into optical or electric (plasma) or thermal energy. Mechanical energy as well as electric, optical, and thermal energies on the contact interface work compositively and the energies affect chemical reactions, resulting in complicated tribochemical phenomena.

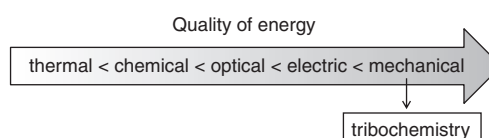


Fig. 2 Energies for chemical reactions

Reactions can be controlled by electrical potential in electrochemical reactions and by light wavelengths in photochemical reactions. Compared to these, tribochemical phenomena are difficult to control. To control tribochemical reactions, the contact surface condition must be kept the same, but it varies from moment to moment due to mechanical contact. It is difficult to predict the thickness of oxide film formed at the contact interface when a 1 kg-steel ball is dropped from the height of 1 meter as mechanical energy. Even if the energy given is accurately controlled, the energy is converted depending on the structure of the contact interface, and its conversion ratio is presumed to depend on the microstructure of the surface. Consequently, unless the conversion process of microscopic mechanical energy in the contact interface is able to be predicted, tribochemical reactions are unable to be accurately predicted. This is the main reason that understanding of tribochemistry and boundary lubrication phenomena is not easy. Surface structure is altered by friction, which makes prediction still more difficult.

4. Causes of Tribochemical Reactions

Because tribochemical reactions are phenomena that occur at contact interfaces, they themselves are complicated. To elucidate complicated phenomena, one must perform factor analysis on the phenomena and investigate the effect of each factor on tribochemical reactions. At an international workshop titled Limits of Lubrication held at Williamsburg, USA, in 1996, we discussed important issues concerning boundary lubrication. One of the issues was tribochemistry. What was summarized at the workshop was that mechanical energy produced various changes on solid surfaces, which were involved in tribochemical reactions. That was, formation of active sites, such as bond scission by frictional heat and shear, lattice defects by deformation, and others. What were taken up as factors included temperature, pressure, lattice defects, nascent surface, radical, exoemission, etc. Classifying this by factors involved in reactions results in reaction conditions and active sources formed on the solid surface as shown in

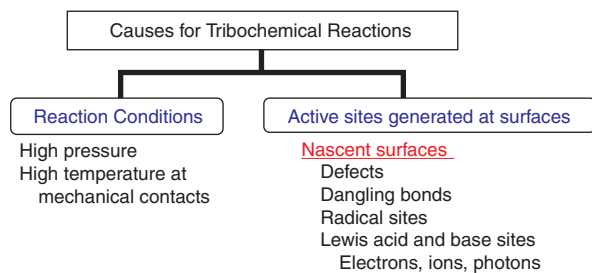


Fig. 3 Causes for tribochemical reactions

Fig. 3. Temperature rise and contact surface pressure at the contact are able to be predicted to some extent by calculation. Consequently, if thermochemical reactions are occurred mainly, reactions are able to be predicted thermodynamically. In this regard, however, actually a number of boundary lubrication results which were unable to be explained by thermochemical reactions were obtained. In the workshop, studies using new techniques were desired to elucidate the relevant factors. In this paper, the chemical activity of the nascent surface is focused and the results by the methods of the authors are introduced.

5. Nascent Surface

Metals are used as tribomaterial, and their surfaces are covered with metal oxides and organic contaminants resulting in the chemically stable surfaces (Fig. 4). In this regard, however, when solid contact occurs under severe lubrication conditions, the surface films are dynamically removed and the metal surface abundant with lattice defects is exposed. This is called nascent surface. The reactions of lubricant components on the nascent surface are assumed to take part in the formation of boundary lubrication film and furthermore boundary lubrication characteristics and efforts have been continually made to find out the chemical properties. For example, an active surface formed by the cutting and synthesis of organic metal compounds⁴⁾ or chemical adsorption of organic acids⁵⁾ have been investigated.

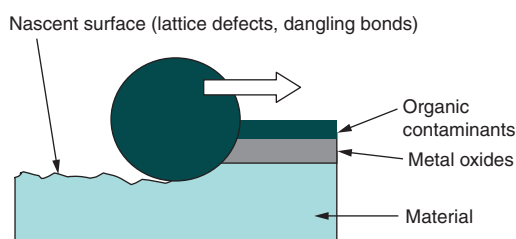


Fig. 4 Surface structure and formation of nascent surface by mechanical stimulation

On the other hand, from the standpoint of surface science, it is difficult to investigate chemical properties of nascent metal surfaces in the atmosphere, and vacuums have been used in the same manner as the technique of catalytic chemistry. Even if the nascent surface is formed under atmospheric pressure, the surface becomes covered with oxide film within a micro second. Consequently, in order to obtain metallic surface without the effects of oxygen or water in the atmosphere, the metallic surface should be prepared under vacuum and their chemical properties have been investigated.

Since Bowden⁶⁾, in order to study boundary lubrication

from the standpoint of surface science, tribological studies have been performed by the use of clean surfaces in a vacuum environment (Fig. 5). In NASA and current JAXA or semiconductor manufacturing technologies, lubrication under a vacuum condition is essential, and vacuums are used for fundamental understanding friction and wear. Recently, high-sensitivity surface analytical tools using vacuums such as electron spectroscopy, etc. have made advances and the relationship between surface structures and tribological characteristics has been clarified.

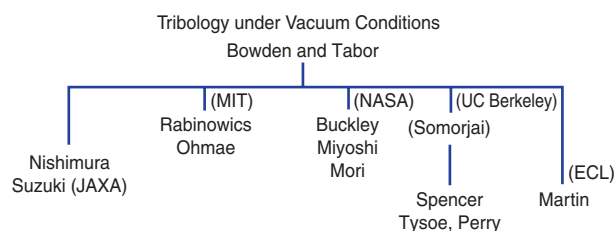


Fig. 5 Researchers who have used vacuum conditions

To clarify tribochemical reactions, vacuums have been used. Specifically, evaporated metal films⁷⁻⁹⁾ prepared in vacuum were used as model surfaces of nascent surfaces. Furthermore, to carry out surface scientific studies, more ideal surfaces have been utilized. They are studies using so-called well-defined surfaces which have been confirmed to be clean by surface analytical tools using highly pure single-crystal metal under ultra-high-vacuum conditions. Because surface reactions during boundary lubrication were difficult to analyze, each of the factors involved in tribochemical reactions were studied in detail under simplified conditions. Furthermore, the relationship between the surface chemical structure and tribological characteristics began to be studied, using advanced surface analyzers such as Auger electron spectroscopy, X-ray photoemission spectroscopy and secondary ion mass spectrometry, etc. Specifically, they were studies of D. H. Buckley¹⁰⁾ et al. and recently, studies of N. D. Spencer or J. M. Martin et al. studies under vacuum conditions have also been conducted in Japan, and studies of Ohmae¹¹⁾ et al. were the most sophisticated studies from the surface scientific viewpoints. As a result of these studies, the elementary step of tribological surface process has begun to be clarified.

On the other hand, a well-defined surface is a kind of ideal surface, and contrivances are required to clarify the tribochemical process that takes place on the actual surface. As one characteristic of nascent surfaces, they are expected to provide a surface assumed to be in the non-equilibrium state and have chemical activity dependent on lattice defects and other structures because the solid surface is formed by mechanical action. Therefore, the author has formed nascent surfaces by dynamic action called friction while using a simplified environment

called a vacuum and elucidated its chemical activity and, at the same time, investigated the relation to the boundary lubrication. In the following sections, the principle of our method and outlines of the results are described and then tribochemistry is introduced for better understanding of boundary lubrication.

6. Evaluation Method for Chemical Activity of Nascent Surface¹²⁾

A friction test is conducted in a vacuum chamber (inner volume: about 1 L) (Fig. 6). Sample gas is introduced from a variable leak valve, to the chamber evacuated by a turbo-molecular pump, and is continuously evacuated. Friction tests are conducted in the sample gas after the pressure P in the chamber becomes steady (Eq. (1) in Fig. 7) when the inlet gas flow into the chamber is balanced with the outlet gas flow. It is the advantage of this test method that even if a slight residual gas (main component is water) remains in the chamber, new sample gas is constantly introduced, The interactions between the nascent surface and sample gas are able to be investigated with the minimum effect of residual gas. This method is an egg of Columbus in a manner. When the sample gas adsorbs to the nascent surface formed by friction, gas pressure P' lowers (Eq. (2) in Fig. 7). From this pressure change ΔP , the adsorption velocity R_a (molecules/s) is able to be estimated by mass balance (Eq. (3) in Fig. 7). In addition, when gas is formed by reactions on the nascent surface, the gas is able to be detected by pressure rise. Pressure change by each component is able to be monitored, by a mass spectrometer mounted to the chamber, and this method is characterized by separately observing the components of adsorption or reaction product. Figure 8 shows the reaction process of gas molecules on the nascent surface. Molecules adsorbed to the nascent surface formed by friction and molecules formed by surface reactions are monitored by mass spectrometer. This method is similar to Temperature Programmed Desorption (TPD) generally used for surface chemistry. Because TPD analyzes interactions and reactions between adsorbed molecules and the surface from components formed by thermal desorption, this can be called as Thermally Induced Deposition in a manner. Our method is able to observe adsorption and reaction on the nascent surface activated by friction and is able to be called Mechanically (Tribochemically) Induced Adsorption and Reaction, and is a dynamic analysis method of chemical properties of the nascent surface with sample gas used as a probe.

By the equation shown before, the adsorption velocity R_a during friction is able to be obtained by calculation. When the gas pressure is sufficient and the friction velocity is slow, the adsorption velocity is proportional

to the friction velocity, that is, the formation velocity of nascent surface. In such event, since the gradient is the number of adsorbed molecules per unit nascent surface, the active site density of the nascent surface is able to be known quantitatively. When the benzene adsorption on the nascent steel surface was investigated, it was found to be nearly monolayer¹³. This indicates that benzene is chemically adsorbed to the nascent steel surface (Fig. 7).

If chemical adsorption, that is, monomolecular adsorption, is premised, the adsorption process of molecules to the nascent surface formed by friction is the first-order reaction, and the pressure decreases exponentially due to adsorption¹² (Fig. 9(a)). The nascent surface is formed by friction and disappears by chemisorption (Fig. 9(b)). When formation rate balances

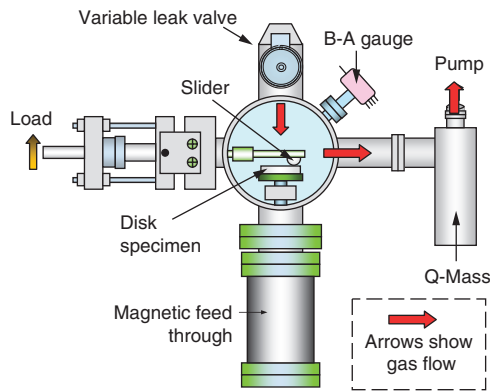


Fig. 6 Schematic diagram of test apparatus for nascent surfaces

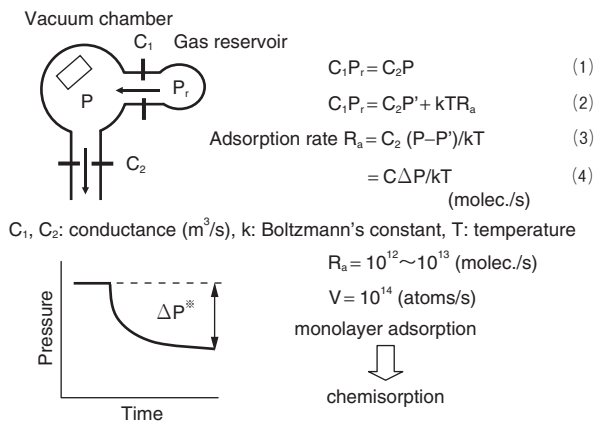


Fig. 7 Mass balance of gas flow and adsorption rate

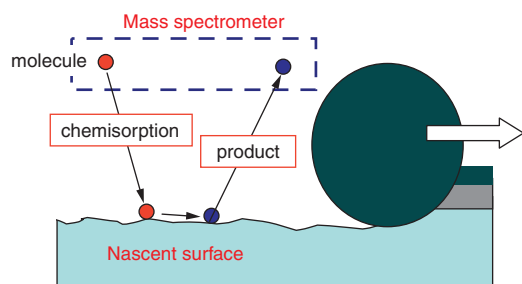
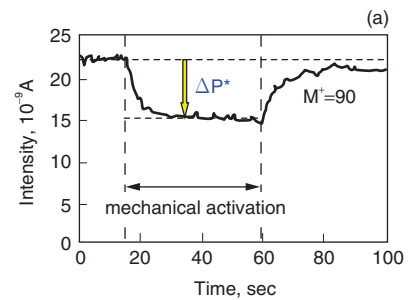


Fig. 8 Mechanically induced chemisorption and reaction

with disappearance rate, the nascent surface becomes steady and the pressure drop in such event is ΔP^* shown in Fig. 9(a). Equation (5) shows the relation of pressure drop with friction time, and as the results show in Fig. 9(c), a good linear relation is obtained. Transforming this equation, we know that the larger the interaction on the surface, the greater the sticking probability¹³, because the gradient of the logarithmic relation is proportional to the sticking probability. The sticking probability is the ratio of molecules to be chemically adsorbed among the molecules that collide against the surface, and shows the strength of interactions between the adsorbed molecules and the surface. We therefore call the gradient c of Eq. (5) "adsorption activity" as a parameter that indicates chemical interaction between the adsorbed molecules and the nascent surface. In general, the adsorption characteristics are evaluated by the adsorption heat, and it is known that the larger the adsorption heat to iron oxides of the oiliness agent, the more improved the wear resistance¹⁴. In such event, this is the adsorption under the conditions of thermal equilibrium, and interactions between iron oxide and oiliness agent molecules are observed. However, the adsorption activity of the nascent surface formed by friction is interaction between the metal surface having lattice defects and the adsorbed molecules, and shows, chemical properties of a surface which is not held thermochemically in equilibrium. Consequently, it is expected that there is correlation



$\ln(1 - \Delta P/\Delta P^*) = -ct$ (5)

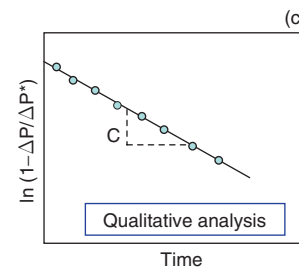
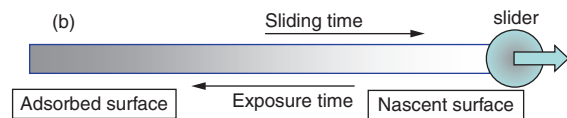


Fig. 9 Time dependence of pressure change and semi-logarithmic relation

between the adsorption activity to the nascent surface and the boundary lubrication characteristics, which will be discussed below.

7. Chemical Properties of Nascent Surface

Chemical properties of nascent metal surface have been described¹⁵⁻²⁰ elsewhere. In this section, their outlines are described. Metal oxides that cover metal surfaces composed of ionic bonds in most cases and have polarity. Consequently, it is well-known that compounds having polar functional groups, for example, fatty acids, amines, tricresyl phosphate (TCP), known as a phosphorus based extreme pressure additive, and others are easy to adsorb. As against this, the nascent metal surface is free of polarity and is considered to have low chemical affinity to compounds with polar functional group as discussed above. What is particularly interesting is that phosphorus-based phosphate ((RO)₃P=O) and sulfur-based alkyl sulfide (RSR and RSSR), which are classified into the same extreme pressure additives, provide completely different adsorbability to the nascent surface. This can be easily explained by the Pearson's Hard and Soft Acids and Bases (HSAB) principle (Fig. 10). That is, Pearson classified acids and bases into hard and soft, and found a principle²¹ that hard-hard or soft-soft combinations easily react. On the other hand, chemical adsorption is a kind of acid-base reactions between the surface and the adsorbed molecule. Compounds having polar functional groups which are hard bases, for example, phosphates, are easy to adsorb on metal oxides which are hard acids. Against this, it is explained that Alkyl sulfide of soft base is easy to adsorb on the nascent metal surface which is a soft acid. Because the active component of steel is the transition metal, iron has a partially un-occupied d-orbital. It is able to be explained that compounds having π-electrons or lone pair electrons are easy to adsorb by donation of the electrons to the d-orbital²². Even in hydrocarbons, which are base oil components, benzene or olefin, which has π-electron, exhibits high adsorption activity, whereas saturated hydrocarbons without functional group (n-hexene and cyclo-hexene) do not adsorb even to the nascent surface. Oxygen, which is a component of air, has high activity, but nitrogen does not adsorb. Water has polarity and provides low adsorption activity to the nascent steel surface.

Figure 10 classifies the adsorption activity of model compounds to the nascent steel surface from the standpoint of lubricant components. Fatty acids and amines known as oiliness agents are hard bases because they have polar functional groups and have weak interactions with nascent surfaces. That is, it should be kept in mind that the oiliness agents having polar functional groups adsorb easily to oxide surfaces and exhibit boundary lubrication

performance, but the oiliness agents exhibit low effect on the nascent steel surface. Fatty acids become soft bases by esterification and esters such as methyl propionate achieve easy interactions with nascent steel surfaces. In addition, phosphates and alkyl sulfides, which are classified as extreme-pressure additives, are compounds having completely different chemical characteristics. As phosphates have polar functional groups and are hard bases, they easily adsorb to metal oxides and have low adsorption activity to nascent surfaces. Against this, alkyl sulfide is a soft base and is easy to adsorb to nascent metal surfaces. The important result²³ is that the chemical affinity to the surface differ between P-based (phosphates) and S-based (alkyl sulfide) EP components.

Aluminum is a representative of non-ferrous metals, but chemical characteristics of the nascent surface considerably differ from those nickel of as transition metal (Fig. 11). Because aluminum does not have a d-orbital, aluminum provides low adsorption to olefin or aromatic compounds, which have π-electron. Oxygen

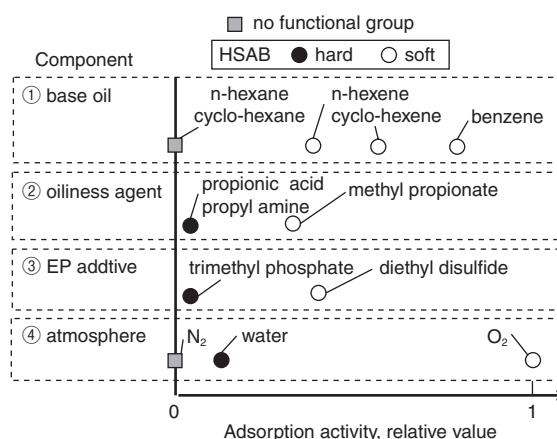


Fig. 10 Adsorption activity of model compounds of lubricant components on nascent steel surface and Pearson's HSAB principle

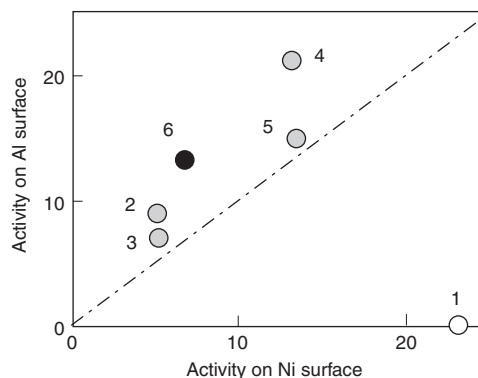


Fig. 11 Comparison of surface activity of aluminum and nickel nascent surfaces for organic compounds 1. benzene, 2. ethanol, 3. n-butyl ether, 4. sec-butyl ether, 5. acetone, 6. ethyl sulfide

containing organic compounds which have lone pair electrons such as alcohol, ether, etc. easily chemisorb to nascent aluminum surfaces. Furthermore, organic sulfur compounds and alkyl halide (RX: X denotes halogen) easily chemisorb to nascent aluminum surfaces, too.

Furthermore, nascent ceramic surfaces exhibited high chemisorption capabilities¹⁶⁾, too. Ceramics of metal oxides, metal nitrides, or metal carbides provide high heat resistance and strength, and are understood to be chemically stable, too. In this regard, however, it is considered that when ceramics bonds are broken by friction, the un-saturated bonds, so-called dangling bonds, are formed, and remarkably high chemical activity is therefore exhibited. As a result of the experiment, high activity that would enable chemisorption was recognized on the nascent ceramics surfaces, even with saturated hydrocarbons which did not adsorb to nascent metal surfaces. Furthermore, even fluorocarbon HFC-134a (CH₂FCF₃) which is chemically stable chemisorbed to nascent ceramics surfaces, and dehydrofluorination, olefin formation, and polymerization of the formed olefin occurred²⁵⁾ (Fig. 12). This can be explained that Lewis acid and base sites were formed on nascent surfaces ceramics, and radical sites were formed by scission of bonds in carbides and nitrides with high covalent characteristics, and they therefore exhibited high activity for polymerization of olefins. This indicates that in even chemically stable ceramics, remarkably active surfaces are able to be formed by breaking the bond mechanically.

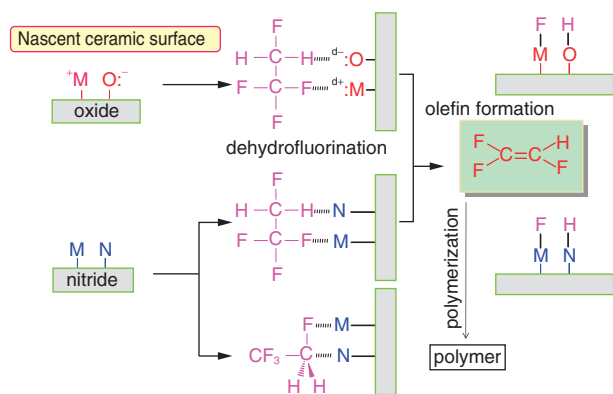


Fig. 12 Chemisorption of CH₂FCF₃ and olefin formation on nascent ceramic surfaces

8. Activity of Nascent Surface and Boundary Lubrication Performance

Based on the chemical characteristics of nascent surfaces discussed above, the action mechanism of the additives in boundary lubrication will be described. The oiliness agents are additives which exhibit lubricity under comparatively mild conditions. It has been explained that when the frictional surface temperature is low, the

oiliness agents adsorb and exhibited lubricity, but when temperature rises, the oil components desorbed and the effect is lost. For example, oiliness effect of fatty acids is recognized in a pendulum test but the effect is unable to be known by a four-ball test. This result is able to be explained by the difference of surface chemical characteristics, though thermal desorption of the adsorbed film is involved. That is, the oiliness agents have polar functional groups and adsorb to oxide films, and therefore, under the mild conditions like a pendulum test, the oiliness agents adsorb to metal oxides on the material surface and exhibit a boundary lubrication property. However, it can be explained that, the effect of the oiliness agents is unable to be obtained, since fatty acids are difficult to adsorb to nascent surfaces formed under severe conditions like a four-ball test.

Extreme pressure additives are generally classified into phosphates (P-based) like TCP and alkyl sulfide (S-based). It has been described that these compounds have different chemical affinity to nascent surfaces (Fig. 10). This result indicates that phosphates like TCP adsorb to oxide films and are easy to form boundary lubrication films, and consequently, under mild conditions in which oxide films remain, TCP exhibits outstanding boundary lubrication characteristics. In addition, TCP would exhibit the effect, under lubrication with boundary films formed on oxide films in advance. Furthermore, when nascent surfaces are exposed to air, oxygen reacts to regenerate oxide films even under severe conditions. However, under the environmental conditions with no oxygen such as in the nitrogen atmosphere or in a vacuum, no effect is obtained with a phosphate like TCP since the oxide films are not regenerated. For example, it has been reported that when TCP is used in the dry nitrogen atmosphere, wear resistance is disappeared²⁶⁾. Against this, alkyl sulfide exhibits EP lubricity under severer conditions²⁷⁾ (Fig. 13), since alkyl sulfide is easy to react with nascent surfaces. Furthermore, it has recently been reported that sulfur-based extreme pressure additives exhibit EP lubricity, in the gear life test under severe conditions²⁸⁾. This can also be explained, that sulfur compounds reacted to the nascent metal surfaces formed under severe conditions.

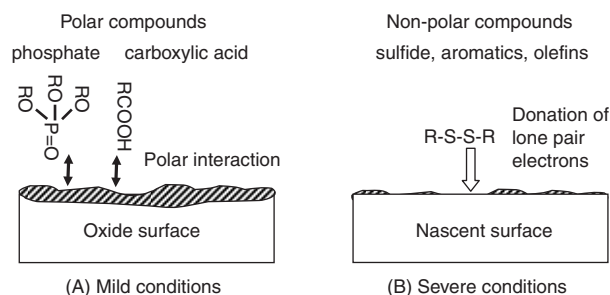


Fig. 13 Surface chemistry controlled by lubricating conditions

Forbes explained the extreme-pressure capabilities of alkyl sulfides, etc. by the thermal reactivity based on the compound structure²⁹⁾. For example, while in the anti-wear region the S-S bond of RSSR breaks to adsorb and exhibits anti-wear property and, temperature rises, in the severe extreme pressure region, and the C-S bond breaks to form metal sulfide which shows extreme-pressure performance. In this regard, however, we have to focus our attention on the fact that nascent surfaces are formed under severe conditions and chemical characteristics of the surface are changed. The results of Forbes can be easily explained if we consider that the nascent surfaces formed under severe conditions react with RSSR directly on the nascent surfaces. In addition, it is reported³⁰⁾ that the use of t-butyl group exhibits superiority in both wear resistance and anti-seizure performance to the use of n-butyl group in the wear resistance test using dibutyl disulfide (BuSSBu: Bu denotes the butyl group), which is a model compound of sulfur based extreme-pressure additives. According to the experiment on adsorption of BuSSBu to the nascent steel surface, it was found that t-butyl exhibited the activity four times as high as n-butyl group¹⁶⁾. This can be explained in that the electron density of the lone pair electrons (S:) on sulfur participating in adsorption is high and t-Bu is easier to chemisorb to nascent surfaces because the electron-donating ability of the butyl group to the sulfur atom is n-Bu < t-Bu. Consequently, this indicates that when alkyl sulfide is used, only changing the alkyl group structure can increase the reactivity to nascent surfaces and can improve the extreme-pressure properties³¹⁾.

With respect to the activity of the nascent surface, studies for investigating the relation with the boundary lubrication have been performed in various fields. Wakabayashi et al. investigated the relation between lubricity and activity of nascent surfaces in cutting work³²⁾. In addition, Shibata et al. reported the relation between lubricity and adsorption on nascent aluminum surfaces in cold rolling of aluminum³³⁾.

In the experiment where ceramics were rubbed in the fluorocarbon HFC-134a atmosphere discussed above,

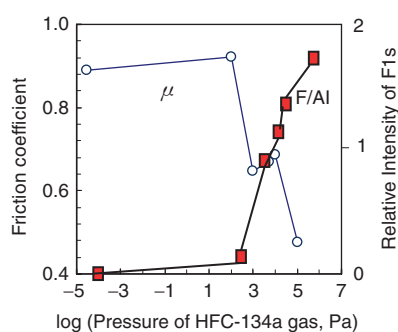


Fig. 14 Effect of partial pressure of HFC-134a on friction coefficient and intensity of fluoride

we showed that fluorocarbon chemisorbed to nascent ceramics surfaces tribochemically. By this reaction, metal fluoride was formed and a friction coefficient drop and improved wear resistance were observed³⁴⁾. As shown in **Fig. 14**, friction and wear lowered from 10³ Pa of partial pressure. An increase of metal fluoride analyzed by XPS well coincided with tribological characteristics improved. This can be explained in that aluminum fluoride generated by tribochemical reactions exhibited lubrication effect as the boundary lubrication film.

Even for the boundary lubrication phenomena which have been difficult to explain only by thermal reactions we can explain them on the basis of chemical characteristics of nascent surfaces. When lubrication conditions or materials are changed in lubrication tests, lubrication characteristics are sometimes difficult to be explained by thermochemical reaction mechanism. In such case, it is suggested that you can try to investigate the boundary lubrication behavior based on adsorption and reactions on nascent surfaces.

9. Tribochemical Decomposition

What has been discussed so far are chemical interactions between molecules of gas and nascent surfaces. Now, do reactions occur when nascent surfaces are formed in the presence of liquid lubricants? Basically, using the same technique as that in **Fig. 6**, friction experiments are performed in a vacuum. Hydrocarbon oil with extremely low vapor pressure for the use in a vacuum (multiply-alkylated cyclopentane: MAC; the molecular structure is shown in the figure) was applied to the bearing steel disk (JIS SUJ2) and friction experiments were performed by the use of a steel ball (JIS SUJ2). As a result, the hydrocarbon oil was decomposed by friction, and hydrogen, methane and other low-molecular weight hydrocarbons as reaction products were detected by mass spectrometer³⁵⁾ (**Fig. 15**). This result indicated that the hydrocarbon oil was decomposed on the friction surface. Because this hydrogen was formed after steel surface was

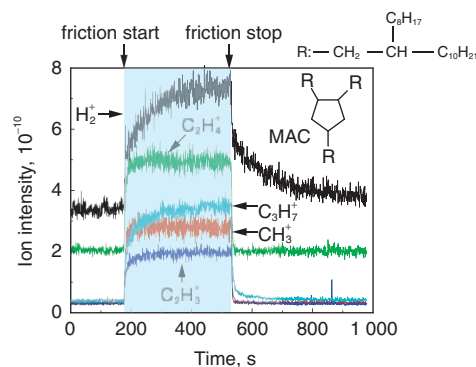


Fig. 15 Gas evolution by tribochemical decomposition of hydrocarbon oil (MAC)

frictioned repeatedly for more than 1km and the oxide film on the steel surface was removed, the nascent surface was apparently involved in the hydrogen formation.

In this regard, however, even when the nascent surface was active, saturated hydrocarbon having no functional group did not adsorb to the nascent surface as shown in **Fig. 10**. Consequently, not only the nascent surface but also frictional heat at the contact region is compositely involved in the decomposition of hydrocarbon oil. When the relation between hydrogen formation by decomposition and contact conditions was investigated, the hydrogen formation rate was proportional to the friction velocity and increased linearly with respect to the cubic root of a load (**Fig. 16**). This indicates that hydrogen formation is dependent on the formation velocity of the nascent surface (active site). As shown in **Fig. 17**, the nascent surface is formed in proportion to the friction velocity V . In addition, the width d of friction scar is the square root of the Hertzian contact area which is proportional to the $2/3$ power of the load. Consequently, the friction scar width, that is, active nascent surface is dependent on the $1/3$ power of the load. What is interesting is that the load dependence in **Fig. 16** does not pass through the origin and has intercepts on the x-axis. Because no decomposition product is detected unless the load exceeds this load, this load was named "critical load."³⁵⁾ The higher the critical load, the more suppressed is the decomposition. Hydrogen formed by tribochemical decomposition of hydrocarbon oil is assumed to be involved in embrittlement of the bearing material, and it begins to be understood that this decomposition reaction can be suppressed by additives.

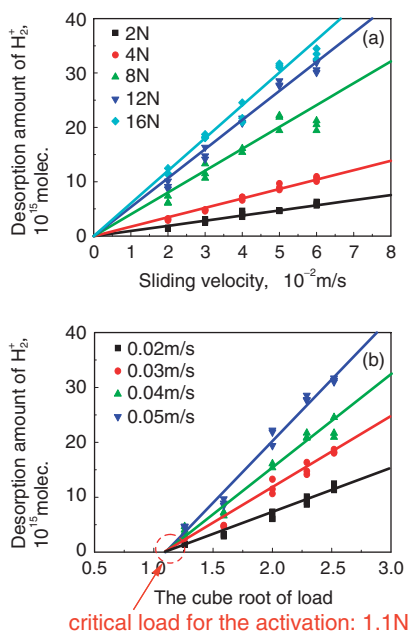


Fig. 16 Dependence of desorption amount of hydrogen on sliding velocity and the cube root of load

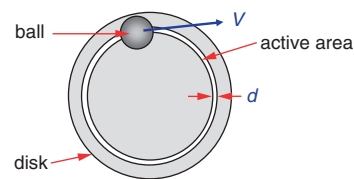


Fig. 17 Parameters for active site formation

10. Conclusion

About 20 years ago, Professor Fischer, already introduced, told the author, "Your researches on nascent surface are interesting but they are not tribology because you did not measure friction and wear simultaneously." In addition, tribologists asked the author, "Is it possible to apply the activity of the nascent surface evaluated in a vacuum to the actual boundary lubrication?" Chemical phenomena under dynamic conditions that occur at the contact interface are complicated and studies in a simplified system are required in order to make clearer the phenomena. The methods introduced in this paper are kinds of the in-situ observation of tribochemical surface reactions. Chemisorption and reaction are detected and surface chemical phenomena are directly observed during friction. The results obtained in a vacuum are evidence in that the actual tribological characteristics can be explained by chemical characteristics of nascent surfaces as described in **Section 8** and the chemical characteristics of nascent surfaces are involved in the boundary lubrication characteristics, though there are gaps between nascent surfaces formed in a vacuum and actual surfaces which are affected chemically by air and oil. In addition, the boundary lubrication phenomena which have been difficult to be understood could be easily explained by the concept of nascent surface. This supports thinking that, nascent surfaces are formed, under severe conditions lubricant components or ambient components competitively adsorb to nascent surfaces and the nascent surfaces are involved in formation of the boundary lubrication films even in actual boundary lubrication. When reactions between nascent surfaces and additives are considered, they have to compete with oxygen and water in the atmosphere, but the reaction of additives is frequently put priority since the concentrations of oxygen and water in lubricants are lower than those of the additives. In addition, the model compounds of lubricants used for evaluation of nascent surfaces have lower molecular weight than that of additives because they are introduced in a state of gas. However, they are assumed possible to be used for evaluation of affinity of additives to nascent surfaces because it is functional groups of molecules that interact with nascent surfaces.

As described before, causes of activity on material surface are compositely involved in tribochemical

reactions. On the contact surface, mechanical energy acts on the solid surface and forms various active sites (**Fig. 3**). By those active sites working compositely, tribochemical reactions take place. Although there are multiple active sources, activity factors are able to be reduced depending on lubricant components, lubrication conditions, materials, and environment. In other words, all we need is to select active sources with attention focused on target lubricant components, lubrication conditions, materials, environment, and contact conditions. For example, it is okay if lubrication phenomena are able to be explained by thermal reactivity with attention placed on the frictional heat, but if not, we would like to seek the causes in active sites on the surface.

Since surfaces are covered with metal oxides when conditions are mild or when the lubricant components are allowed to adsorb to the surface in advance, a molecular structure easy to adsorb to metal oxides should be chosen. However, when conditions are severe and nascent surfaces are formed, attention should be focused on the compounds which have affinity to nascent surfaces. In the action mechanism of additives under particularly severe contact conditions, chemical activity of nascent surfaces would be involved. When the surface which is covered with adsorbed additives is machined, the adsorption film to the oxide surface would exhibit good lubricity. This is the reason why the lubricant component is chosen according to conditions. In addition, when the material is changed, the lubricant components should be chosen depending on chemical characteristics of the nascent material surface. As shown in **Fig. 11**, chemical characteristics of the nascent surface greatly differ between steel and aluminum. Competition adsorption of lubricant components and environment components such as humidity must be taken into account. Because tribochemical reactions in the friction interface depend on lubricant components as well as materials, contact conditions, and environment conditions, the boundary lubrication characteristics should be understood with the effect of these factors.

Professor Tanaka says, "... it is difficult to say that the boundary lubrication model is presented as a mathematical expression model that enables quantitative prediction of performance" as compared to fluid lubrication³⁶. Although there is the boundary lubrication model by Bowden-Tabor the structure (=mechanical properties) and the coverage of the boundary lubrication film are determined by tribochemical reactions at the contact interface. Furthermore, since tribochemical reactions are determined by multiple factors, prediction of boundary lubrication film is extremely difficult and it is not a model that can be used for tribological design. Qualitative understanding of tribochemical phenomena would progress but we have still a long way to go to

reach the tribological design through quantitative control of tribochemical reactions. In this regard, however, if we change our point of view, we know that various reactions occur by combinations of materials, lubricant components, etc. and this suggests that, there still remain lots of seeds which enable us to find tribochemical reactions resulting in technological renovation in the world of boundary lubrication. We are able to approach new technologies through understanding new tribochemistry without being possessed with textbooks and old common knowledge, and tribochemistry could be said a world which awaits our reclamation. If readers find this paper useful for their understanding and technological development of boundary lubrication, our goal will have been achieved.

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