

Surface Chemical Aspects in Boundary Lubrication

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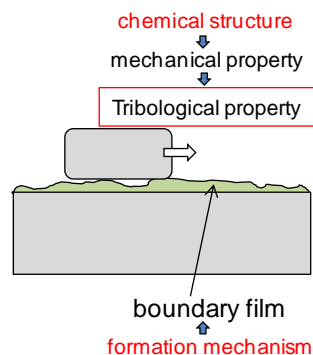
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Graphical abstract



Abstract

Boundary lubricating behaviors were investigated from the viewpoint of surface chemistry based on our results. Boundary lubricating properties are closely related to the chemical structure of boundary lubricating films. TOF-SIMS (time of flight secondary mass spectroscopy) which has several advantages such as high sensitivity, high spatial resolution and high chemical resolution was applied to chemical analysis of boundary lubricating films. Degradation of lubricating films on hard disk media was investigated by TOF-SIMS and removal of the lubricant oil and chemical wear of slider materials was observed. It was found that the tribochemical degradation of the oil was catalyzed by the slider material such as Al_2O_3 and TiN. The degradation was suppressed when DLC and c-BN were used as a slider material. Thin layer of PTFE on tribo-material composed of PTFE-PEEK was characterized by TOF-SIMS after lubrication tests with a steel ring. It was found that the surface coverage of PTFE was decreased with increasing contact pressure from 6 to 27 MPa and welding occurred when the surface coverage was less than 20%. A tracer method with stable isotopes such as $^2\text{H(D)}$, ^{13}C and ^{18}O was introduced for characterization of boundary layer formed from organic additives. Effectiveness of chemisorbed ethyl alcohol-d5 ($\text{CD}_3\text{CD}_2\text{OH}$) for lubrication of CrN with alcohol was confirmed by TOF-SIMS analysis. An important role of nascent surfaces on tribochemical reactions to form boundary layers was investigated. For the reaction of EP additives, an organic sulfide was more reactive on nascent steel surface than organic phosphates. It was found that decomposition of synthetic hydrocarbon oil was catalyzed by nascent surface of steel under the effect of frictional heat.

Keywords: Surface chemistry; boundary lubrication; surface analysis; TOF-SIMS; nascent surface; tribochemical reaction

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1.0 INTRODUCTION

Surface chemistry plays an important role in the fundamental understanding of advanced technology such as catalysis, material science and so on. In 2007, Prof. Ertl has received the Nobel Prize for his basic studies of chemical processes on solid surfaces, relating to modern surface chemistry such as fuel cells, artificial fertilizers and clean exhaust. Boundary lubrication is also related closely to surface chemistry, because boundary lubricating properties are controlled by the chemical structure of boundary lubricating films which are formed on lubricating surfaces through tribochemical reactions from lubricant components, tribomaterials and atmospheric components at mechanical contacts.

There are two important roles of surface chemistry on boundary lubrication, namely, (1) chemical analyses of boundary lubricating films of which structure affects tribological properties and (2) formation mechanism of boundary films formed by tribochemical reactions at mechanical contacts. In this paper, boundary lubricating behaviors will be reviewed from the viewpoint of surface chemistry based on our studies

2.0 TOF-SIMS ANALYSIS OF BOUNDARY LUBRICATING FILMS

Boundary films are composed of adsorbed and reacted layers on tribomaterial. Since the thickness is order of nanometer, boundary films have been analysed by structure-sensitive surface analytical tools [1, 2] such as XPS, AES and so on. Tribological properties in boundary lubrication are closely related to the mechanical property of boundary films which is dependent on the chemical structure of the films. Therefore, it is important to investigate the chemical structure of boundary films to understand boundary lubrication behaviors as shown in Figure 1. There are many analytical tools which are characterized by resolutions as shown in Figure 2 (Tools with an open square have an advantage that surface analysis can be carried out under air). EPMA with SEM is popular to investigate tribosurfaces with high resolution of surface morphology and provides two dimensional distribution of elements. AES is more sensitive to detect elements on the outermost surface than EPMA and has a high two-dimensional resolution. AFM has an atomic scale resolution two-dimensionally, but chemical information is not available from AFM.

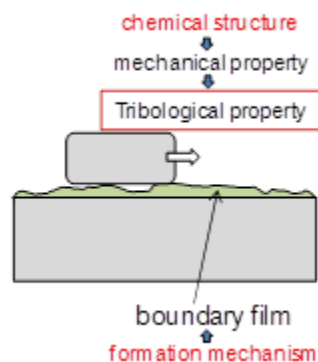


Figure 1 Surface chemical aspect on boundary condition

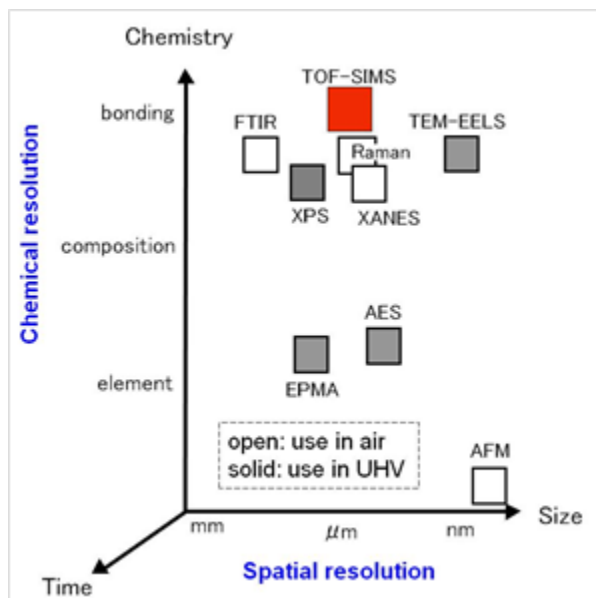


Figure 2 Tools for surface analysis with high resolution

Recently, TOF-SIMS has been developed as a sensitive analytical tool to characterize surface chemical structure. TOF-SIMS has several advantages to analyse chemical structure of tribosurfaces, (1) high sensitivity: it can detect atoms and molecules at the amount less than monolayer, (2) high spatial resolution of $1\mu\text{m}$ and (3) it can characterize chemical species. Since TOF-SIMS has an extremely high mass-resolution, chemical bond structures of surface layers can be analysed precisely. Therefore, we have been investigating chemical structure of nano-tribofilms using TOF-SIMS. Selected results will be shown below.

Media surfaces of hard disks are covered with several nm of hard coating(DLC) and 1 nm of lubricant film to obtain better tribological performance of head-disk interface(HDI). The life and reliability of HDI are guaranteed by the thin lubricant film. The lubricant is perfluorinated polyether(PFPE) oil with high thermal stability. It was found that the oil decomposed tribochemically during sliding tests even under a mild condition(98 mN, 35 mm/s) [3], although the oil has an excellent thermal stability. Therefore, the decomposition mechanism and the effect of slider materials on the decomposition reaction were investigated using TOF-SIMS.

Sliding experiments were carried out under an extremely mild condition(0.8 mN, 10 mm/s) in the main chamber of TOF-SIMS⁴⁾. Friction tracks were investigated with TOF-SIMS just

after termination of sliding experiment. A typical result is shown in Figure 3. The mass spectrum and the chemical image of CF^+ as a fragment ion of the lubricant oil, show the loss of lubricant from the friction track even under the mild condition mentioned above. It can be concluded that the lubricant oil was decomposed chemically during sliding experiments. From a high resolution mass-spectrum, aluminum ion was detected only inside of friction track as shown in Figure 4. The aluminum ion was concentrated in the friction track as shown in the chemical image of Al^+ in Figure 5. These results indicate obviously that the aluminum ion was transferred from Al_2O_3 slider. This result shows that Al_2O_3 was reacted tribochemically with PFPE oil resulting in the formation of AlF_3 which was detected at the friction track by TOF-SIMS.

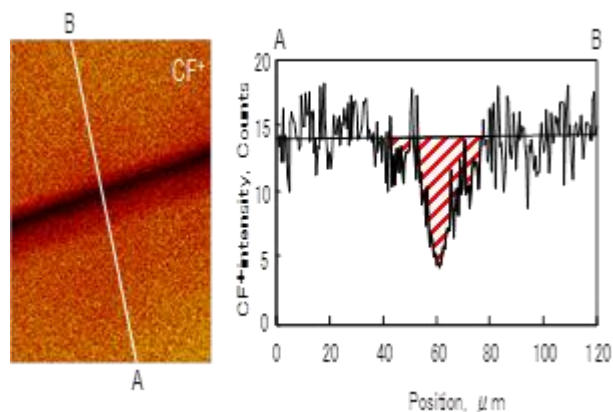


Figure 3 Chemical image and cross-section of ion intensity by TOF-SIMS

The amount of the lubricant loss during sliding test was estimated from a cross-section of the intensity of CF^+ or C_2F_4^+ ion along to the line A-B as shown top of Figure 4. It has been reported that the tribochemical decomposition of PFPE oil was affected by slider materials [3]. Therefore, the effect of slider materials on the decomposition reaction was investigated. Sliders coated with hard layers such as DLC, c-BN, TiN and Al_2O_3 were used for sliding experiments. It was found that the oil removal was accelerated with Al_2O_3 and TiN sliders compared to DLC and c-BN sliders. Since Al_2O_3 and TiO_2 as a surface oxide of TiN are known as Lewis acid, PFPE oil could be decomposed catalytically by the oxides. Since DLC and c-BN are made of a covalent bond and have no acid site on their surfaces, lubricant loss was decreased by using DLC and c-BN. In conclusion, DLC and c-BN coatings have a better tribological performance to extend longer life of head disk interface. Currently, both surfaces of head and disk are covered with DLC, hard and chemically inert coating to obtain a longer life of HDI as shown in Figure 6.

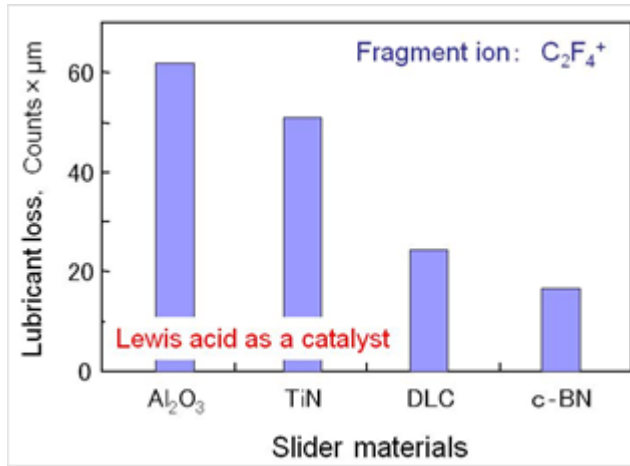


Figure 4 Catalytic effect of slider coating on decomposition of PFPE oil during friction tests

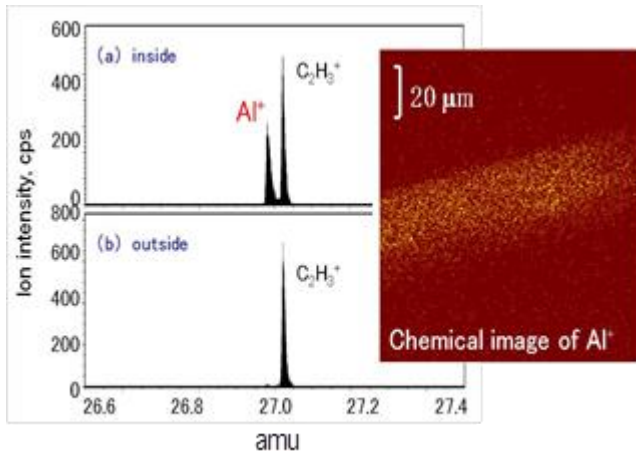


Figure 5 High resolution mass spectra and chemical

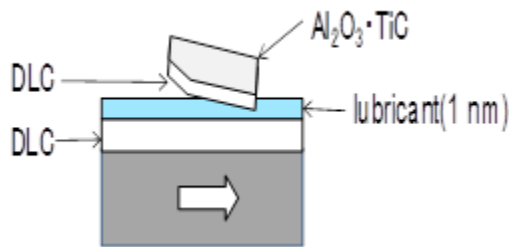


Figure 6 DLC coating for long life of HDI

A composite material of PTFE-PEEK which is composed of polytetrafluoroethylene (PTFE) particles as a solid lubricant in poly ether-ether ketone (PEEK) matrix has been used as a bearing material to obtain low friction coefficient. A load carrying capacity of PTFE-PEEK was investigated from the viewpoint of surface chemistry [4]. Figure 7 shows chemical images of CF⁺ fragment ion from PTFE on the material surfaces after lubrication tests under different contact pressure. The surface before lubrication test is entirely covered with thin layer of PTFE which was confirmed from a mass spectrum of friction track. It is obvious that the material surface was covered with PTFE film, because the mass peaks at 50 amu intervals which are the

fragment ion of CF₂⁺ were observed in the mass spectrum. The intensity of CF⁺ ion in the chemical image decreased when the lubrication tests were carried out at higher contact pressure as shown in Figure 7. The surface coverage of PTFE is estimated from a relative intensity of CF⁺ ion. The coverage decreased with increasing contact pressure as shown in Figure 8. When the coverage was decreased less than 20%, seizure was observed. This result shows that PTFE thin layer acts as a solid lubricant but was removed during lubrication tests at higher contact pressure. Finally, seizure occurred at lower PTFE coverage. In addition, it was found that PTFE coverage could be recovered when lubrication test continued at lower contact pressure.

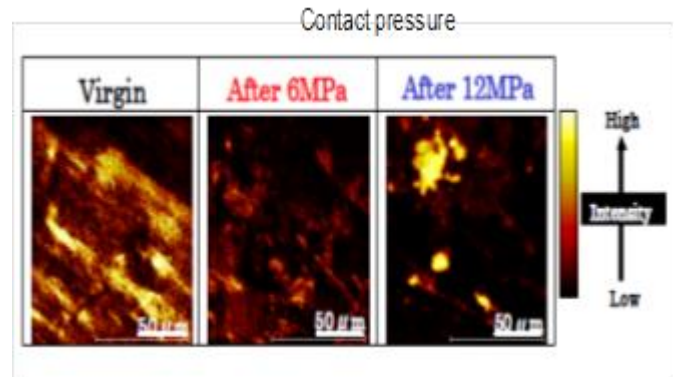


Figure 7 Chemical images of PTFE-PEEK surface after friction tests

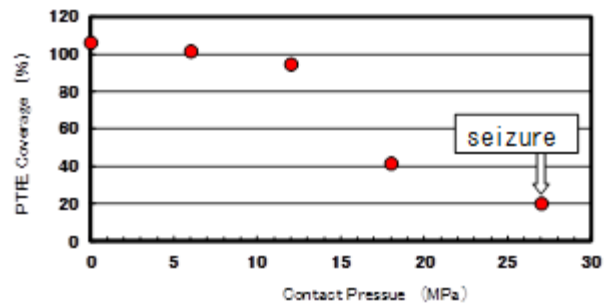


Figure 8 Relation between surface coverage of PTFE and contact pressure

Chemical analysis of boundary films formed with lubricant additives such as over-based calcium sulfonate, organic phosphate and organic sulfide by TOF-SIMS has been reported elsewhere [5].

TOF-SIMS can be applied for a tracer method as shown in Figure 9. Since many lubricant components are made of C, H and O, surface lubricant layers are also composed of C, H and O. In this case, it is difficult to analyze chemical structure of boundary layers because surfaces are always covered with organic contaminants. If lubricant components contain stable isotopes such as ²H(D), ¹³C and ¹⁸O, it is easy to detect the components on friction track without disturbance of organic contaminants by using TOF-SIMS. One of the results is shown below. Ethyl alcohol has been investigated as a lubricant for nitride ceramics such as CrN and TiN [6]. The result of lubrication test was shown in Figure 10. Obviously, ethyl alcohol is more effective as lubricant for CrN than TiN. A boundary layer should be formed on CrN surface during lubrication tests. Therefore, deuterated ethyl alcohol (CD₃CD₂OH, ethyl alcohol-d₅) was used as a tracer, and the fragment ion of CD₃CD₂O⁻ ion was detected at the

friction track of CrN at higher intensity compared to TiN as shown in Figure 11.

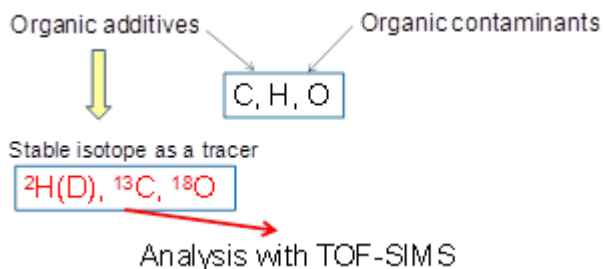


Figure 9 TOF-SIMS tracer methods with stable isotopes

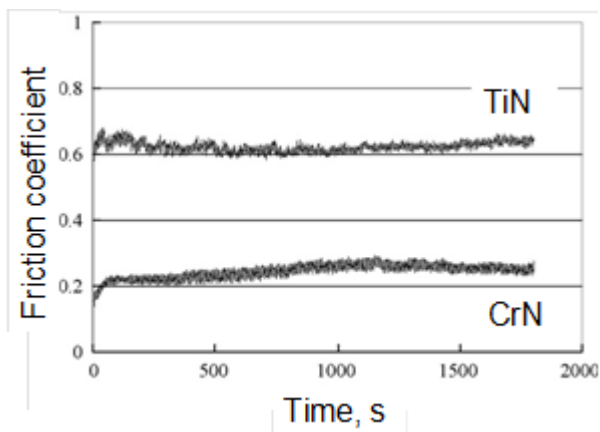


Figure 10 Lubrication property of ethyl alcohol

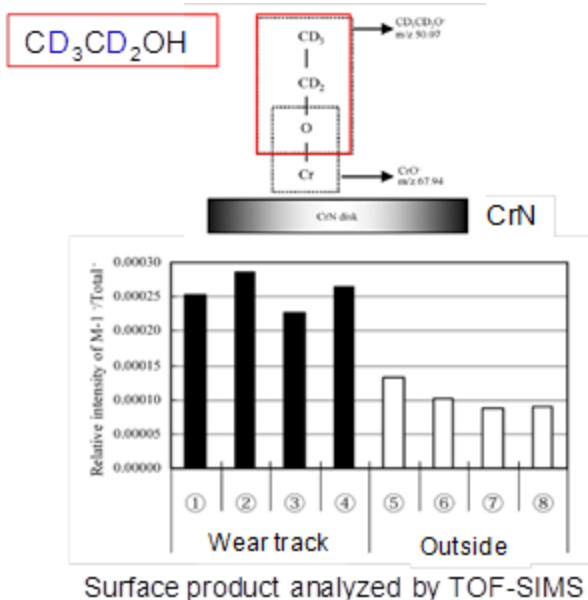


Figure 11 Chemisorbed alcohols on friction track of CrN

The intensity of the D-fragment ions on TiN was less than half of the intensity on CrN and the ion intensity on TiN was not observed difference between inside and outside of friction track. The result clearly shows that chemisorbed layer of ethyl alcohol on CrN acts as a boundary layer.

3.0 TRIBOCHEMICAL REACTIONS ON NASCENT SURFACES

Boundary lubricating properties are controlled by the mechanical properties of boundary films which are formed by tribochemical reactions at sliding contacts. The structure of products as a boundary film is controlled by tribochemical reactions of lubricant components and tribomaterials. Therefore, tribochemical reactions should be investigated in order to understand boundary lubricating properties fundamentally.

The mechanism of tribochemical reaction is complicated, because the reactions occur under the effect of mechanical energy. The main causes and sources of tribochemical reactions are divided into two factors as follows, (1) the extreme conditions such as high temperature and high pressure at mechanical contacts and (2) active sites formed on tribomaterials by mechanical contacts. Lattice defects, nascent surfaces, radical sites and exoemissions have been reported as the surface active sites. The active sources and causes mentioned above are concerned to tribochemical reactions in a complicated way. Therefore, we have to investigate the role of the active sources in tribochemical reactions separately.

Clean metal surfaces prepared in ultra-high vacuum have been used as a model of nascent metal surfaces [7, 8]. However, nascent metal surfaces should have high activity, because they have surface defects formed at mechanical contacts. Therefore, we have been studying on the important role of nascent surfaces on the tribochemical reactions of lubricant components and have developed a unique method to investigate chemical nature of nascent surfaces [9, 10]. In this paper, chemisorption of lubricant additives and decomposition reaction of base oil component on nascent steel surfaces will be focused on. Experimental apparatus is shown in Figure 12. A friction tester is installed in a vacuum chamber and nascent surface is formed by friction under flow of a sample gas. Adsorption of sample gases on nascent surface and desorption of reaction products are monitored by a quadrupole mass spectrometer. The rate of chemisorption and product formation can be estimated from pressure change of the gases by friction.

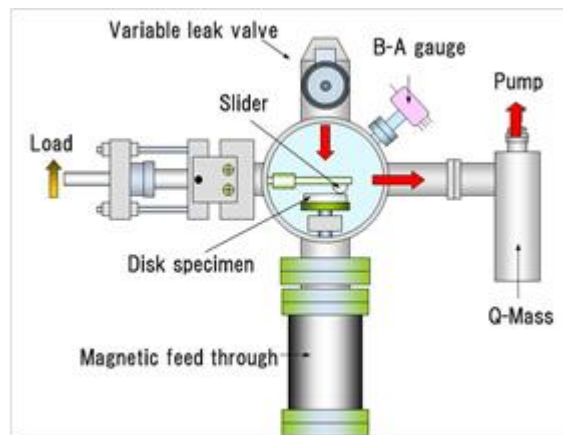


Figure 12 Apparatus for characterization of chemical nature of nascent surfaces

In general, material surfaces are covered with metal oxides and organic contaminants under mild conditions and then the surface is stabilized chemically by them. Once the surface films are removed by mechanical contacts at severe conditions, chemically active surfaces, so-called nascent surfaces, are formed

as shown in Figure 13. Since nascent surfaces have a lot of surface defect, chemical activity of nascent surfaces is expected to be high. We have found that nascent gold surface is so active that benzene chemisorbed on it and decomposed even at room temperature [11].

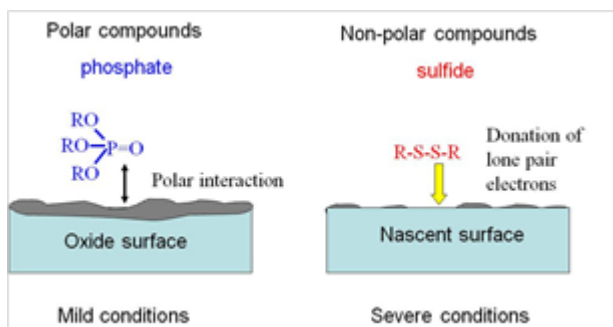


Figure 13 Chemical affinities of EP additives with oxide-covered and nascent surface

Chemical nature of nascent steel surfaces was characterized by our method as follows. Aromatics and olefins which have π -electrons chemisorb easily on nascent steel surface. This can be explained by the donation of π -electrons to a vacant d-orbital of transition metal. Surface defects such as steps and kinks are recognized as a surface active site. Nascent steel surfaces show a high chemical activity, because they have a lot of surface defect formed by mechanical contacts [12, 13].

Polar compounds such as carboxylic acids and amines which chemisorb easily on metal oxide surfaces show relatively low adsorption activity on nascent steel surface. Therefore, oiliness agents such as fatty acids are expected to be effective on oxide-covered tribomaterials under a mild condition.

Although organic sulfides and organic phosphates are well-known as an extreme pressure additive, their reactivity on nascent steel surface is extremely different [14]. Organic phosphates have a polar functional group and interact with oxide surfaces easily, but it is difficult to interact with nascent steel surface for phosphates. On the other hand, organic sulfides chemisorb easily on nascent steel surface by the donation of lone pair electrons on sulfur to nascent steel surface. Therefore, it can be concluded that organic phosphates are effective on oxide-covered surface under mild conditions and organic sulfides are more effective on nascent surface formed under severe conditions rather than mild conditions as shown in Figure 13. In conclusion, we should select a suitable additive based on the surface chemistry which is dependent on lubricating conditions in order to obtain a better lubrication performance.

It was found that evolution of hydrogen and hydrocarbons [15] with low molecular weight such as ethane was observed by Q-mass during lubrication test with synthetic hydrocarbon oil as shown in Figure 14. This indicates that base fluids can decompose easily under synergy effect of nascent steel surface and temperature rise at sliding contacts as shown in Figure 15. The reaction was accelerated linearly with increasing sliding speed and a third power of load that is the formation rate of nascent surface. Since hydrocarbon gases such as n-hexane do not chemisorb even on nascent steel surface, saturated hydrocarbons do not interact chemically with nascent steel surface [14]. The decomposition reaction shown in Figure 11 can be explained by a synergy effect of nascent surface and temperature rise at sliding contact.

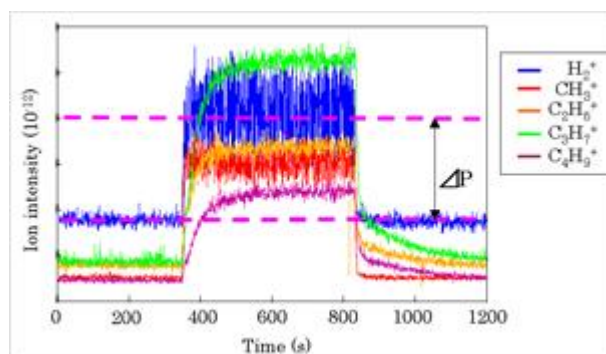


Figure 14 Gas evolutions during lubrication test with synthetic hydrocarbon oil on steel

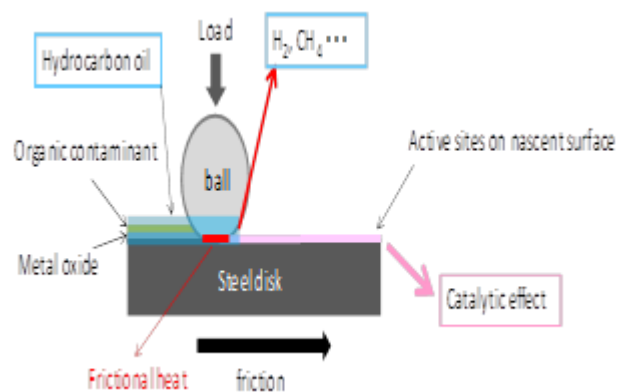


Figure 15 Synergy effect on nascent surface and frictional heat on decomposition of lubricant oil

The decomposition reaction was inhibited by additives. It is noteworthy that organic phosphates are more effective than organic sulfides to inhibit the tribochemical decomposition reaction [16].

4.0 CONCLUSION

The important role of surface chemistry to understand boundary lubrication was reviewed from the viewpoints of chemical analysis of boundary layers and tribochemical reaction of lubricant components.

Boundary lubricating properties are closely related to the chemical structure of boundary films which can be characterized by surface analytical tools. In this paper, TOF-SIMS which has high resolutions of amount, spatial and chemical structure was introduced as a powerful tool to investigate chemical analysis of boundary films. TOF-SIMS can be applied to investigate boundary films from monolayer to hundreds of nm. Chemical images of fragment ions provide two-dimensional information of chemical species around friction track. A tracer method with stable isotopes makes it possible to detect lubricant components without disturbance by organic contaminants.

Since boundary films are formed through tribochemical reactions at sliding contacts, it is important to understand the reaction mechanism. There are several active sources and the role of nascent surfaces was focused on. Chemisorption behavior of additives is controlled by surface chemical nature which is altered by mechanical contacts. Lubricant components interact chemically with material surface to form boundary layers. Under

mild condition, surface is covered with metal oxide and polar compounds such as fatty acid and organic phosphates can chemisorb easily. On the other hand, the surface layers such as oxide and organic contaminants are removed under severe condition and nascent surfaces are formed. In this case, non-polar compounds such as aromatics, olefins and organic sulfides chemisorb more easily than polar compounds. Therefore, it can be concluded that lubricant components should be selected according to surface chemistry which is dependent on lubricating conditions. It is important to know the chemical structures of sliding contacts to obtain fundamental understanding of boundary lubrication characteristics.

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