A Novel Tool for Mechanistic Investigation of Boundary Lubrication: Stable Isotopic Tracers

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1. Introduction

1.1 Surface analyses of tribological surfaces

It is well understood that lubrication modes can be classified into three categories. Under hydrodynamic conditions, two rubbing surfaces are ideally separated by liquid film derived from lubricating oil. Therefore, the surface chemistry of the rubbing parts is of less importance. When the operational conditions become severe, for example, under conditions of increased load, the rubbing surfaces come in contact. This is defined as the boundary lubrication condition. Under these conditions, the properties of solid surfaces are important. There is an intermediate mode between hydrodynamic lubrication and boundary lubrication; namely mixed lubrication. Direct interaction between surfaces may occasionally take place under these conditions. Tribo-chemistry controls the performance of mixed lubrication and boundary lubrication conditions [1].

Challenges to understanding the surface chemistry of rubbed surfaces by tribologists using instrumental analyses started as early as the 1960s. Tribo-active elements such as phosphorus and sulfur were found by electron-probe microanalysis (EPMA) of rubbed surfaces lubricated with mineral oil containing additives [2]. These reports clearly support the tribo-chemical reaction of anti-wear and extreme pressure additives (AW/EP). In the 1970s, Auger electron spectroscopy (AES) was introduced as a more surface sensitive tool in tribology [3]. EPMA and AES are frequently applied in tribo-chemistry as useful tools. However, these instrumental analyses are elemental analyses of solid surfaces that identify only the elements that exist on the surfaces.

When FeS, FeS_2, and $FeSO_4$ were analyzed, EPMA and AES detected sulfur in the sample but could not identify the chemical states of the sulfur found. X-ray photoelectron spectroscopy (XPS) provides different chemical shifts between iron sulfide (FeS) and iron sulfate ($FeSO_4$) in S 2p spectra [4]. X-ray absorption near edge structure (XANES) identifies iron monosulfide (FeS) and iron disulfide (FeS_2) [5]. These surface analyses mainly detect inorganic compounds. Although carbon is detectable, chemical resolution of carbon by these tools is not always sufficient for identifying the structure of organic compounds in detail.

SIMS has been introduced as another surface sensitive instrumental analysis in tribology [6]. Contrary to AES, EPMA, XANES, and XPS, SIMS does not provide any chemical information regarding the sample directly [7]. It provides the molecular weight of substances that exist on surfaces. On the other hand, it detects all substances that can be ionized by a primary ion. Both organic and inorganic compounds can be analyzed by SIMS.

Therefore, it is a potentially versatile tool for tribo-chemistry in which organic compounds are the major contents in lubricants. One of the most important features of SIMS, and the main subject of this work, is to detect elemental isotopes. The principle of SIMS analysis is described in detail in the following section.

Nomenclature

Abbreviation	Description
AW/EP	anti-wear agents and extreme pressure additives
$C_{18}NH_2$	octadecylamine, $C_{18}H_{37}NH_2$
$C_{18}OH$	octadecyl alcohol, $C_{18}H_{37}OH$
D	deuterium, ^2H
DLC	diamond like carbon
GMO	glycerol monoleate, 2,3-dihydroxypropyl 9(Z)-octadecenoate
m/z	mass to charge ratio
OA-D35	perdeuterio-octadecanoic acid, $C_{17}D_{35}COOH$
OA-H35	octadecanoic acid, $C_{17}H_{35}COOH$
PAO	poly(alpha-olefin)
SIMS	secondary ion mass spectroscopy

1.2 Application of isotopes in tribo-chemical investigation

Isotopes are defined as elements that have the same atomic number but have different mass numbers [8]. For example, hydrogen has three isotopes; they are protium (^{1}H, usually expressed as H unless otherwise stated) having the mass number of 1, deuterium (^{2}H, usually abbreviated as D) having the mass number of 2, and tritium (^{3}H, usually abbreviated as T) having the mass number of 3. The difference in mass number is attributed to the difference in the number of neutrons in the nucleus (Figure 1). Among the three isomers, protium and deuterium are stable isotopes and tritium is a radioactive isotope. Usually, isotopes behave chemically in a similar manner. Therefore, they can be used as tracers in chemical processes if they were effectively detected. Radioactive isotopes are easy to detect using a Geiger counter, even if a small amount exists in the sample. Taking advantage of this high detectability, radioactive isotopes were applied in tribo-chemistry of AW/EP additives before surface analyses were introduced. For example, ^{35}S-labeld organic sulfides were employed as AW/EP additives in mineral oil. Radiation from solid surfaces was detected after rubbing with the labeled lubricants. These results clearly indicate that tribo-chemical reactions of sulfur occurred during rubbing [9]. However, radioactive isotopes are considered to be biological hazards and are difficult to handle. Another limitation of this technique is that it provides merely elemental analysis of surfaces. Therefore, radioactive isotopes are not frequently applied in tribo-chemical investigation.
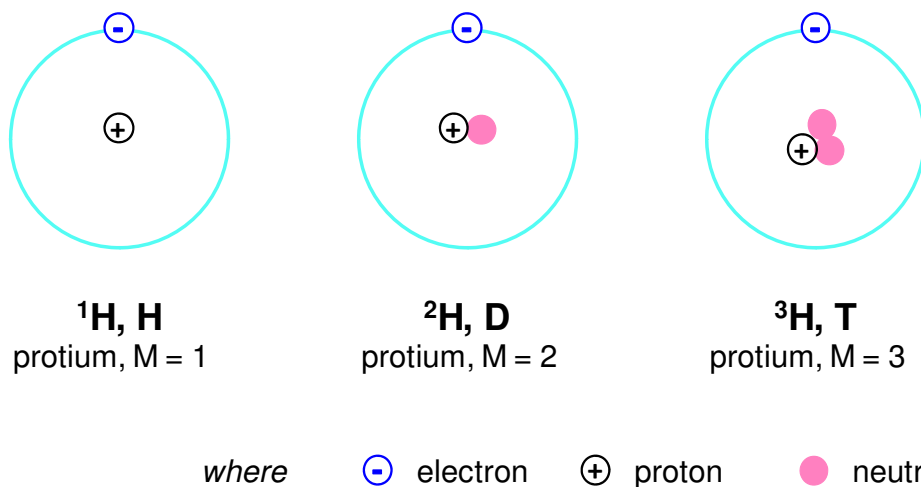
Fig. 1. Schematic model of hydrogen isotopes

Stable isotopes exist everywhere and are not considered to be biological hazards. For example, hydrogen is comprised of ^1H and D, and the latter is the minor isotope found in nature. Also carbon is comprised of ^{12}C and ^{13}C, where the later is the minor component (Table 1). High resolution instrumental analyses such as mass spectroscopy can detect and identify these minor isotopes. This led us to expect that additive molecules, which are the minor component in lubricants, could be detected by identifying stable isotopes. In this concern, model lubricants that are enriched with minor isotope(s) (D or ^{13}C) would improve the detectability of a target molecule by instrumental analyses.

Element	Isotope	Mass number	Numbers of		Abundance, atom%
			proton	neutron	
Hydrogen	^1H	1	1	0	99.985
	^2H	2	1	1	0.015
Carbon	^{12}C	12	6	6	98.9
	^{13}C	13	6	7	1.10
Oxygen	^{16}O	16	8	8	99.76
	^{17}O	17	8	9	0.04
	^{18}O	18	8	10	0.20

Table 1. Natural abundance of isotopes for hydrogen, carbon, and oxygen

1.3 Principle of SIMS analysis

SIMS consists of mass spectroscopy that measures the weight of the molecules in a sample. However, we cannot measure the weight of molecules directly even using an ultra high sensitive balance. Note that the weight of one molecule of water is as light as 3×10^{-23} g. Instead, mass spectroscopy measures the weight of ions. That is, mass spectroscopy ionizes a molecule in a sample followed by separation of generated ions according to m/z. Understanding of the ionization process of a sample is key to successful analysis. In SIMS, as schematically illustrated in Figure 2, irradiation of a primary ion such as Ga^+, Au^+, Bi^+ to the target molecule yields secondary ion(s). If the molecule was simply ionized by exchanging electron(s) with the primary ion (without scission of any chemical bond existing in the molecule) this process yields molecular ion $[M]^+$ or $[M]^-$, where M is the formula weight of the sample molecule. This gives a signal of m/z M in the mass spectrum. Most organic compounds contain C–H bonds. For these compounds, scission of a C–H bond usually occurs during the ionization process. If a proton (H^+) migrated from the original molecule, it yields an $[M-H]^-$ ion, which causes the loss in the formula weight by one. By contrast, if hydride (H^-) migrated, it results in a $[M-H]^+$ ion. Since the mass number of hydrogen is 1, the migration process gives m/z M–1 and m/z 1 in the mass spectrum. The migrated proton or hydride are active species and they react with the original molecule that yields $[M+H]^+$ or $[M+H]^-$, respectively. Therefore, the ion of m/z M+1 is frequently found in the mass spectrum of organic compounds. In mass spectroscopy, $[M]^+$ and $[M]^-$ ions are defined as molecular ions. Similarly, $[M-H]^-$, $[M-H]^+$, $[M+H]^+$, and $[M+H]^-$ are defined as quasi-molecular ions. These ions are used to identify the sample by its formula weight.
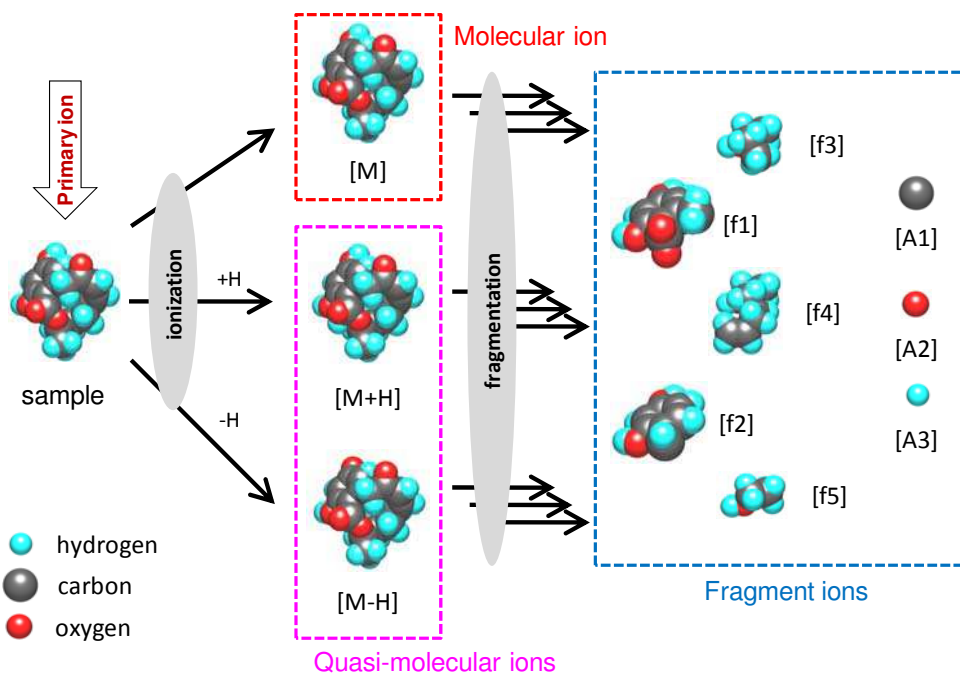

Fig. 2. Generation of secondary ions and the fragmentation in SIMS

Scission of C–C bonds or other bonds (such as C–O) also happens during the ionization process. As a result, the C-C skeleton is destroyed to several moieties. This is defined as fragmentation that yields fragment ions (for example, [f1]–[f5] in Figure 2). The fragmentation is a multistep process; it proceeds further and finally yields atomic ions (for example, [A1]–[A3] in Figure 2). Thanks to the fragmentation of molecule, mass spectroscopy is able to identify atoms that exist in the sample as well as partial structures and functional groups present in the molecule. However, the fragmentation is usually a complicated process. Patterns of fragmentation for typical compounds are available on a database [10]. However, this approach seems insufficient for tribology because tribo-chemistry deals with a complex mixture as lubricants. One of the solutions to this problem is to compare the mass spectrum of sample with that obtained from the authentic sample(s).

A quantitative analysis is possible by SIMS according to the intensities of the ions. For this purpose, the conversion of ionization influences the reliability of the results. Some molecule or moieties therein easily ionize, but others do not. For example, organofluorides provide high intensities of fluorine-containing fragments, according to our experience. Sources of primary ions and their energy are the important factors for quantitative analysis in SIMS.

As already mentioned, SIMS does not provide chemical information of samples directly, but provides only the weight of ions. For example, octadecanoic acid (stearic acid, $C_{17}H_{35}COOH$), which is a well studied model friction modifier, provides m/z values of 283 and 285 as quasi-molecular ions in the mass spectrum. Hydrocarbons that have $C_{21}H_{32}$ moieties are able to provide m/z 283 and 285 as fragment ions. They yield the same quasi-molecule ions in the m/z spectrum. As a result, there are several possible chemical structures that meet the value of m/z. Careful study of the mass spectrum according to the fragmentation of the sample molecule is the usual method in SIMS to identify a molecule. However, tribology deals with complicated mixtures of additives as a solution in base oils. Since the fragmentation of each compound is also complicated, as discussed above, SIMS of tribological surface usually results in a chaotic spectrum. Therefore, novel techniques are highly desired for tribo-chemical research. Taking these fundamental aspects into account, we were inspired to use stable isotopes for tribo-chemistry. Stable isotopes usually behave in a similar manner chemically. Synthesis of model lubricant molecule that labeled with stable isotope(s) is possible. SIMS can trace the molecule during tribological processes by paying attention to the isotopes. This idea provides simple and clear results through the tribo-chemical process.

2. SIMS study of lubricants on surfaces

2.1 Monomolecular layer on nonrubbed surface [11]

Straight-chain fatty acids such as octadecanoic acid are one of the best studied friction modifiers. They reduce the friction between steel/steel contacts when they are added to hydrocarbon oils. The formation of densely packed, well-oriented adsorption films had been widely accepted as their lubrication mechanism [12]. In fact, the monomolecular layer of octadecanoic acid deposited on flat metal surfaces provided low friction [13].

This work began with the simple comparison of the SIMS spectrum of natural octadecanoic acid ($C_{17}H_{35}COOH$, OA-H35) and deuterio-labeled octadecanoic acid ($C_{17}D_{35}COOH$, OA-D35). Thus, the monomolecular films of OA-H35 and OA-D35 were deposited on the Si(100) surface by means of the Langmuir–Blodgett trough [14]. Surface coverage by the adsorbed area was measured by the surface force. As shown in Figure 3, both OA-H35 and OA-D35 provided similar monomolecular films. The SIMS spectrum of OA-H35 (formula weight of 284) deposited on the surface is shown in Figure 4. Quasi-molecule ions at m/z 283 and at
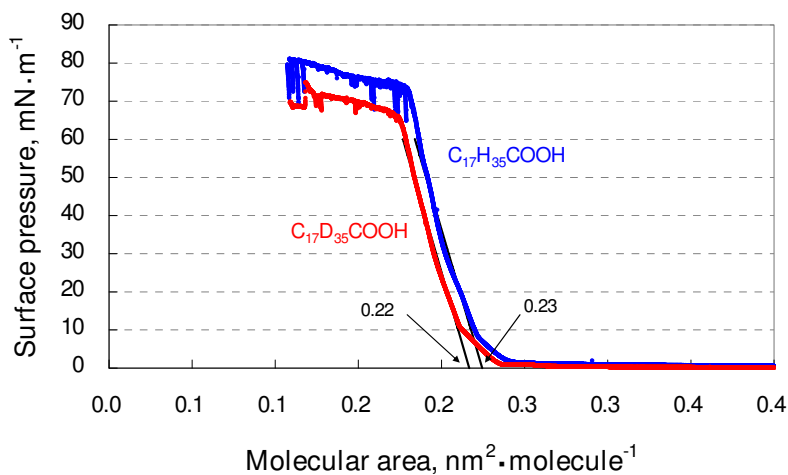
Fig. 3. Diagram of molecular area and surface pressure during the preparation of monomolecula film from octadecanoic acids
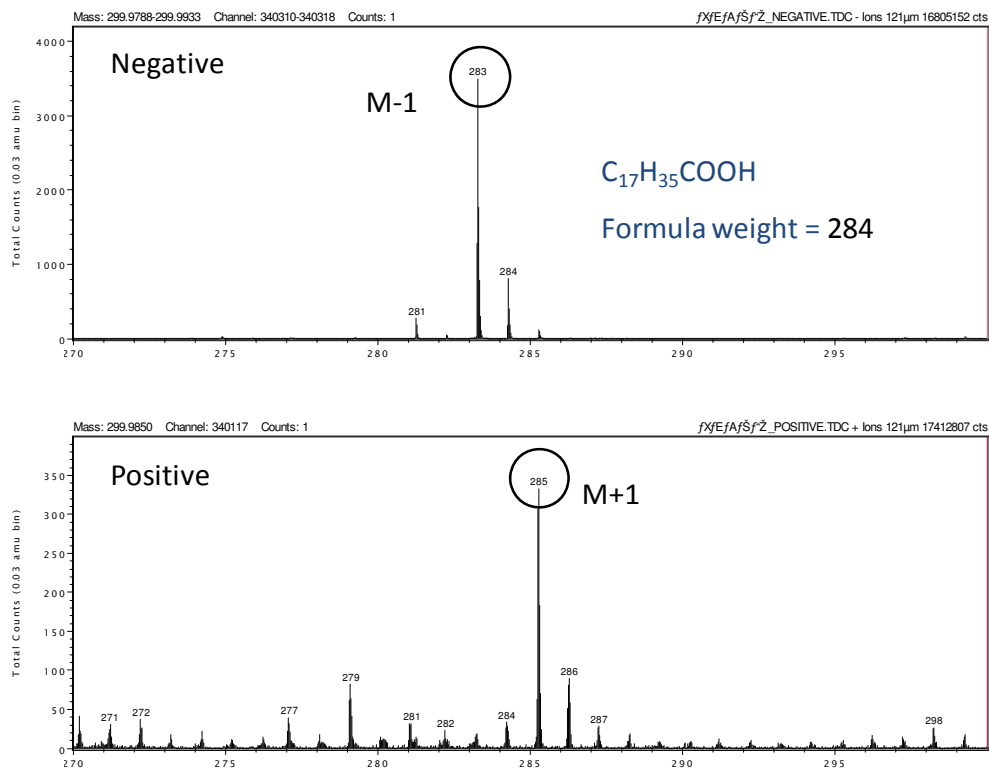

Fig. 4. SIMS spectra of OA-H35 on the Si surface (m/z 270–300)

m/z	Relative intensity, -
284	100
285	20
286	2.4
287	0.17

Table 2. Intensity of molecular ions derived from octadecanoic acid; calculation based on the natural abundance of isotopes

285 that correspond to the [M-H]$^-$ and [M+H]$^+$ ions respectively were found with high intensities. In addition to these ions, strong signals for negative ions at m/z 284 and positive ions at m/z 286 were also found. These ions are reasonably explained by natural isotopic abundance, as shown in Table 2. Also this table indicates quasi-molecule ions of small signals at m/z 285 in the negative spectra and at m/z 287 in positive spectra.

The SIMS spectrum of OA-D35 (formula weight of 319) provided quasi-molecular ions at m/z 318 in the negative spectra and at m/z 321 in the positive spectra (Figure 5). It is interesting that the m/z of the positive quasi-molecule increased by two from the formula weight of the original molecule, while the m/z of negative quasi-molecular decreased by one from the formula weight of the original molecule. These results can be explained by the mechanism of fragmentation as shown in Figure 6. The migration of the acidic proton (hydrogen in COOH group) from the original carboxylic acid yields a carboxylate anion, which corresponds to a negative quasi-molecular fragment ion [M-H]$^-$ and a proton H$^+$ (path A in figure 6). The protonation of the original carboxylic acid (coordination of COOH to the proton) yields an oxonium type cation, which corresponds to a positive quasi-molecular fragment ion [M+H]$^+$ (path B in Figure 6). Not only the acidic hydrogen but also the hydrogen of the alkyl group migrates during the fragmentation process. This process with OA-D35 yields a deuterium cation (D$^+$) with the mass number of two. Then the coordination of the original acid to the deuterium cation yields an oxonium type cation, which corresponds to a positive quasi-molecular fragment ion [M+D]$^+$ (path C in Figure 6). Therefore, the increase in m/z by two for quasi-molecular ions can be applied as a fingerprint of deuterium labeled compounds.

Further fragmentation yields atomic ions and small size fragment ions. Figure 7 shows positive mass spectra of m/z from 1 to 20. The reference OA-H35 provided fragment ions of m/z 1, 12, 13, 14, and 15, which correspond to H, C, CH, CH$_2$, and CH$_3$, respectively. Obviously, OA-D35 provided different mass spectrum from that of OA-H35: m/z values of 1, 2, 12, 14, 16, and 18, which correspond to H, D, C, CD, CD$_2$, and CD$_3$, respectively. A considerable intensity of H at m/z 1 was observed in the mass spectra of OA-D35. A plausible explanation is the high conversion of ionization of the acidic proton in OA-D35. This also explains the considerable high intensity of [M+H]$^+$ quasi-molecular ions in the mass spectra of OA-D35.
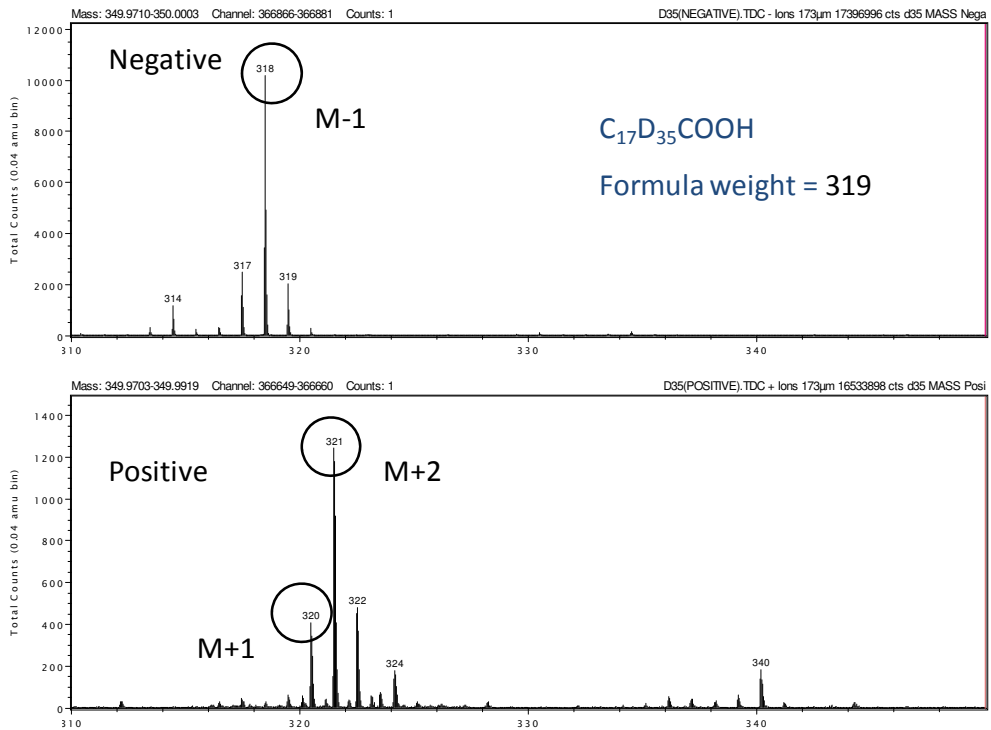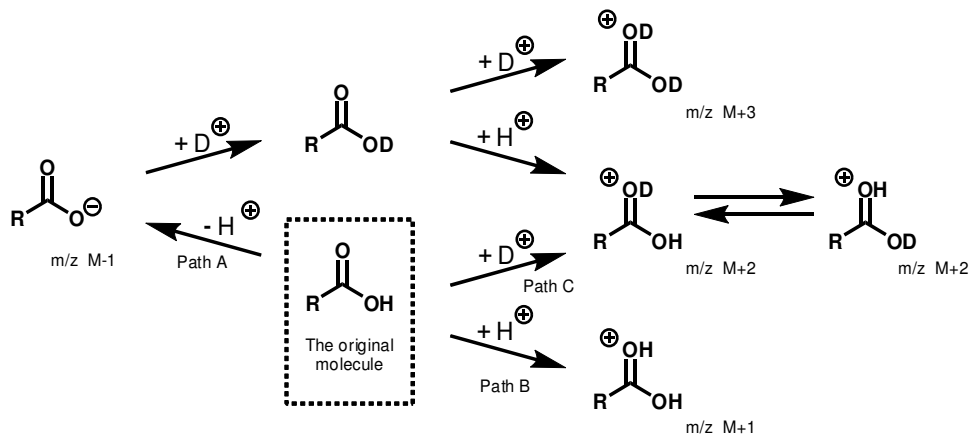
Mass: 349.9710-350.0003   Channel: 366866-366881   Counts: 1   D35(NEGATIVE).TDC - Ions 173µm 17396996 cts d35 MASS Nega

Negative

M-1

$C_{17}D_{35}COOH$

Formula weight = 319

Mass: 349.9703-349.9919   Channel: 366649-366660   Counts: 1   D35(POSITIVE).TDC + Ions 173µm 16533898 cts d35 MASS Posi

Positive

M+2

M+1

Fig. 5. SIMS spectra of OA-D35 on the Si surface (m/z 310–340)

where M = formula weight of the original acid

Fig. 6. Generation of quasi-molecular ions from carboxylic acids
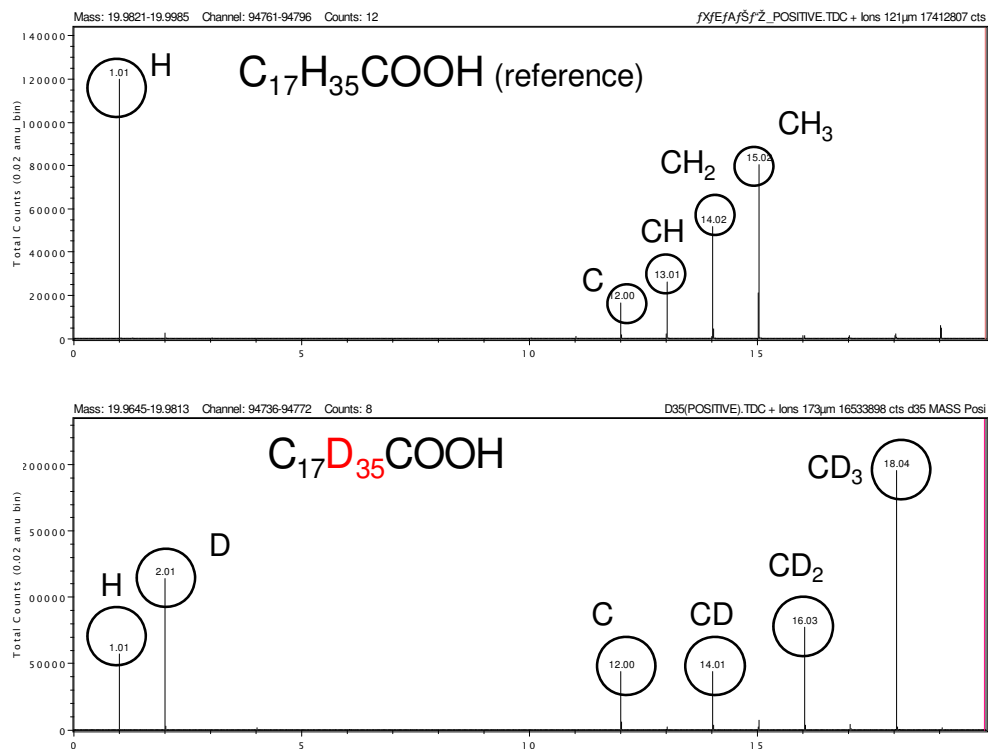
Fig. 7. SIMS spectra of OA-H35 and OA-D35 on the Si surface (m/z 0–20)

2.2 SIMS analysis of rubbed surface covered with monomolecular film [15]

A sapphire ball was slid against a monomolecular film of OA-D35 on a flat Si surface for 50 s at a load of 40 mN. Then, chemical mapping around the rubbed surface was obtained, as shown in Figure 8. The intensity of m/z 28 (Si) increased whereas that of m/z 2 (D) decreased after the tribo-test. Also, the intensity of m/z 27 (Al) increased to some extent. On the ball surface (Figure 9), the intensity of m/z 2 increased and that of m/z 27 decreased. These results can be explained by the removal of the monomolecular film from the flat surface by rubbing. This results in the exposure of Si, which is the base material of the flat surface. The transfer of OA-D35 (removed from the monomolecular film) onto the ball and the transfer of aluminum containing material (worn off from the ball) onto the flat surface took place by rubbing. Changes in surface chemistry by rubbing were also studied by quantitative analysis of the flat surface across the wear track. The intensity of m/z 2 and 28 inside the wear track are clearly different from those outside the wear track. The intensity of m/z 27 inside the wear track slightly increased.

AFM (atomic force microscope) analysis of flat surface around the wear track indicates the differences in the height between the outside and inside of the wear track is approximately 2 nm (Figure 10). Since the molecular size of OA-H35 is 1.8 nm in length, the AFM analysis supports the removal of the monomolecular film from the Si surface. There was a border
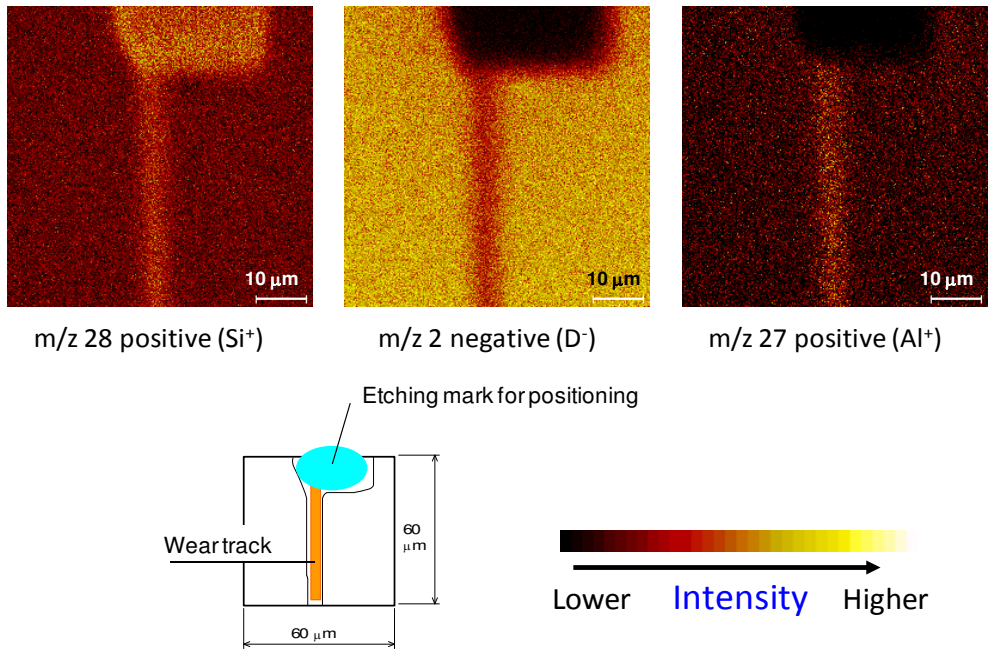
m/z 28 positive (Si$^+$)   m/z 2 negative (D$^-$)   m/z 27 positive (Al$^+$)

Fig. 8. Chemical mapping of the silicon-flat obtained by SIMS (rubbed against a sapphire-ball for 50 s)

m/z 28 positive (Si$^+$)   m/z 2 negative (D$^-$)   m/z 27 positive (Al$^+$)
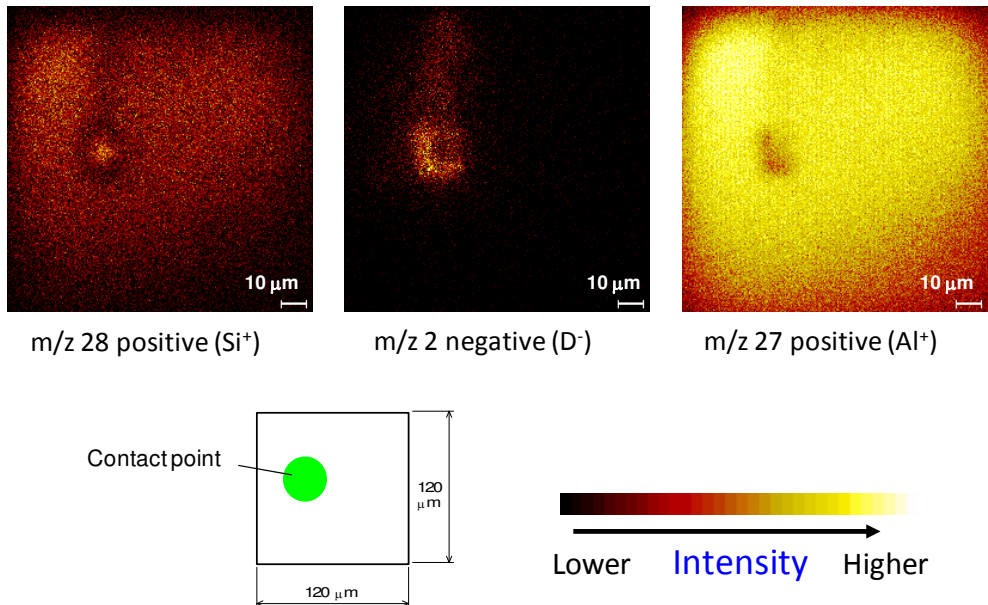
Fig. 9. Chemical mapping of the sapphire-ball obtained by SIMS (rubbed against the silicon surface for 50 s)
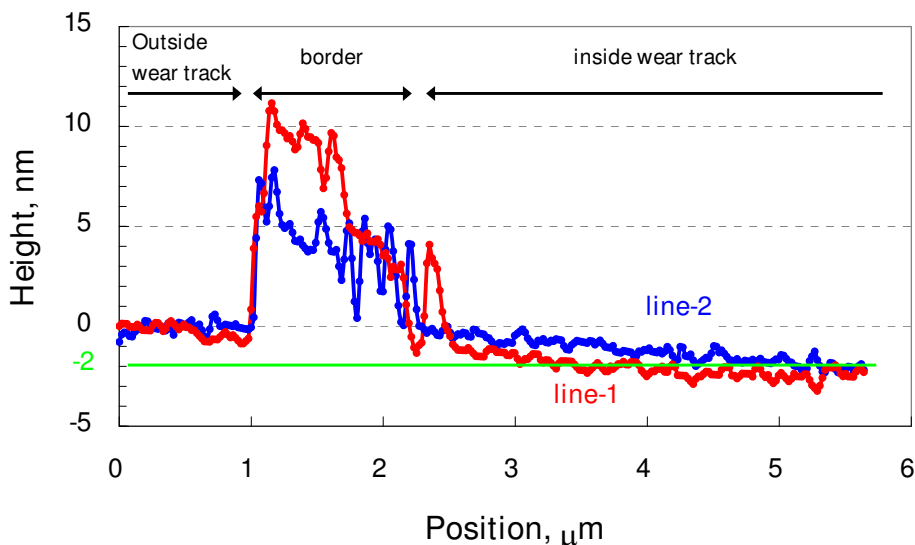
Fig. 10. Profile of the silicon-flat obtained by AFM (rubbed against a sapphire-ball for 50 s)

area between the inside and outside of the wear track. This area is characterized by its considerable height. We are greatly interested in the chemistry of the border area. However, AFM cannot detect any differences in the chemistry of the sample. Unfortunately, the spatial resolution of the SIMS apparatus employed in this work was not sufficient for the small sample area. Wear particles from the tribo-materials and removed OA-D35 might have accumulated during the tribological process. Anyway, we can detect changes in chemistry by rubbing using deuterium labeled lubricant and SIMS analysis of the resultant surface. It should be noted that evidence of wear down to the nanometer level was detected by this technique.

2.3 Influence of tribo-material on the durability of monomolecular films

Steel, sapphire, and glass balls were slid against a silicon surface covered with a monomolecular film of OA-D35. The influences of the ball material on the lifetime of the monomolecular film were observed obviously, as shown in Figure 11. The friction force of the steel ball rose within the test duration of 100 s (2000 cycles). A sapphire ball provides a longer lifetime, approximately 2,100 s. A glass ball provided an excellent lifetime of more than 10,000 s [16]. The glass ball provided a low friction coefficient of approximately 0.06 throughout the tribo-test. The results can be explained by low contact pressure (0.62 GPa for the steel ball, 0.71 GPa for the sapphire ball, and 0.47 GPa for the glass ball) and the good affinity of the carboxylic acid for the ball material. The steel ball also provided a low friction coefficient of 0.06 at the steady state, but the duration was short. The sapphire ball gave a higher friction coefficient in the range of 0.07–0.09. A slight increase in friction during the test with sapphire was observed.

The results of surface analyses suggested the role of the transferred acid onto the ball surface from silicon surface. Pretreatment of the steel ball was conducted to examine the lifetime of the monomolecular film. A fresh ball was rubbed against the monomolecular film
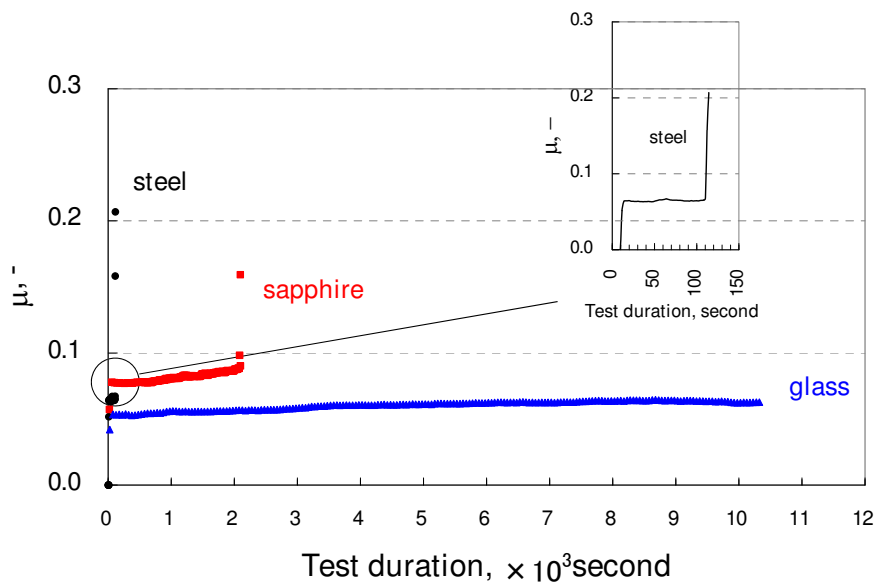
Fig. 11. Effect of the ball material on the durability of the monomolecular film
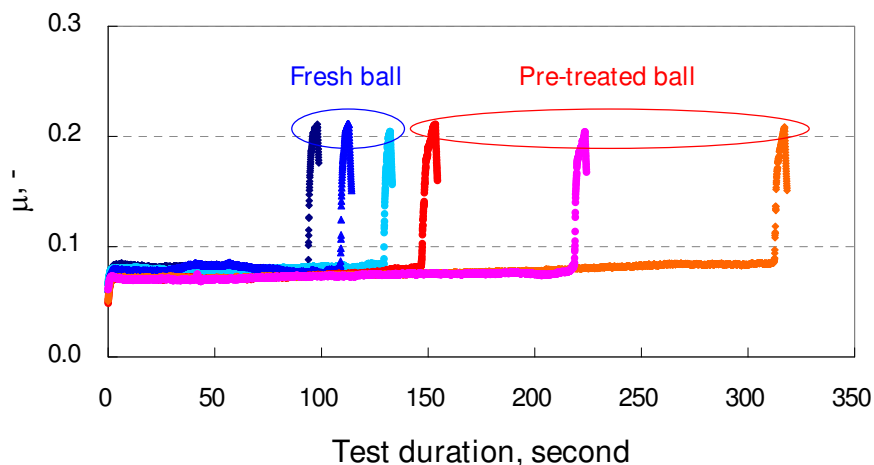

Fig. 12. Effects of pretreatment of the ball surface on the durability of the monomolecular film

deposited on the Si for 10 s (200 cycles). Since the lifetime of the combination of the steel ball and the monomolecular film was 95–130 s (Figure 12), the pretreatment was finished within the lifetime of the monomolecular film. Then, the pretreated ball was slid against a new track on the silicon surface. The pretreatment resulted in 50%–300% improvement in the lifetime [16]. Both surfaces were covered with OA-D35 if a pretreated ball was slid on a new track. This enhances the durability of the monomolecular film for lower friction. However, optimization of the pretreatment has to be investigated.

Taking these results into account, we wish to propose the following mechanism of lubrication by the monomolecular film as expressed in Figure 13. At the initial stage of the tribo-test, OA-D35 on the Si surface was removed by the mechanical stress. A transferred film composed of the acid would be generated if the removed acid adsorbed on the ball surfaces. This leads to a long lifetime of the film with low friction. On the other hand, degradation of the monomolecular film of OA-D35 followed by insufficient generation of the transferred film on the ball surface causes high friction and short lifetime in friction reduction. It was suggested that the affinity of the carboxylic acid in the ball material influences the transfer phenomena.
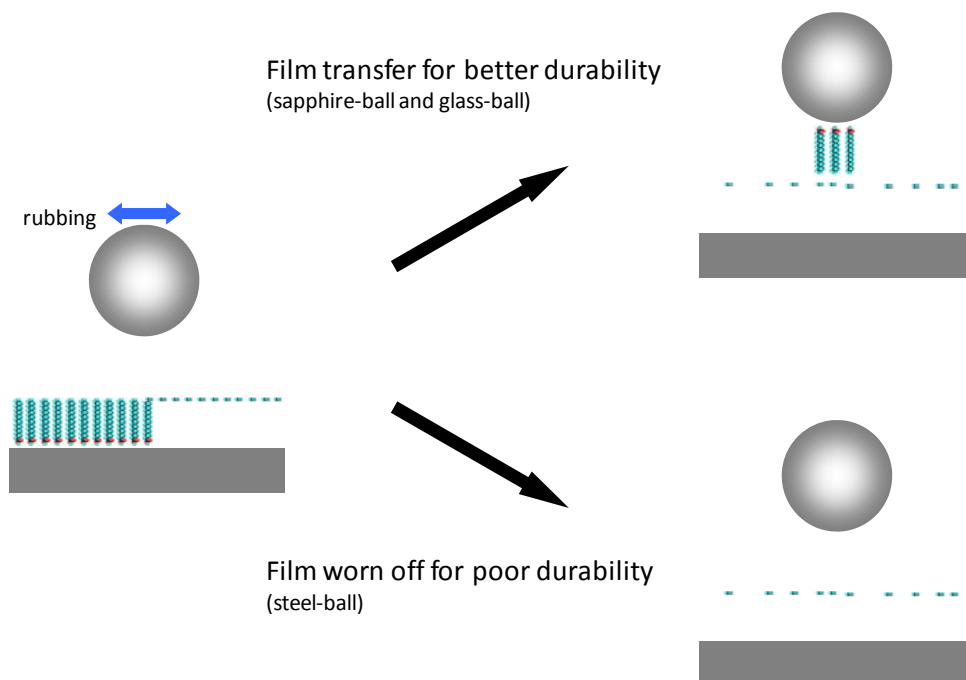

Fig. 13. A proposed mechanism for the durability of the monomolecular film

2.3 The tribological properties of a binary-component monomolecular film [11]

A binary-component monomolecular film was deposited from the equimolecular mixture of octadecylamine ($C_{18}H_{37}NH_2$, $C_{18}NH_2$) and OA-D35 or octadecyl alcohol ($C_{18}H_{37}OH$, $C_{18}OH$) and OA-D35. The tribological properties were obtained by sliding a steel ball against the film. The binary-component film with $C_{18}NH_2$ provided high friction and short durability, while that with $C_{18}OH$ provided low friction and was fairly durable, as shown in Figure 14. Chemical mapping of the flat surface after the tribo-test for 100 s is shown in Figure 15. For the $C_{18}NH_2$ + OA-D35 binary system, the intensity of the total positive ions on the rubbed area was much greater than those of the nonrubbed area. Careful analysis of the chemical image revealed that the increase in intensity of total ions due to increases in the fragment ion of m/z 28 (Si). At the same time, decreases in the intensities of m/z 2 (D), 270 ($C_{18}NH_2$), and 318 (OA-D35) were observed. The results indicate that the binary-component film was worn off by rubbing.
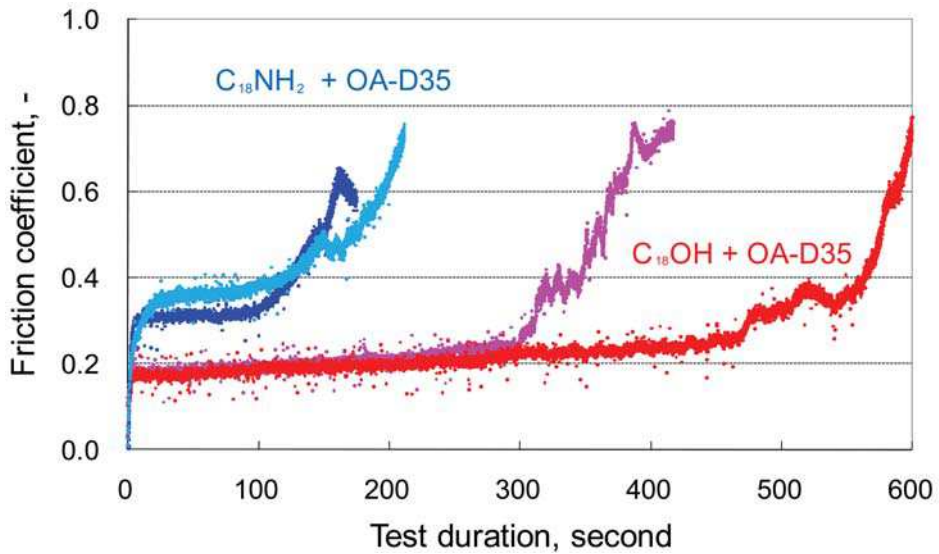
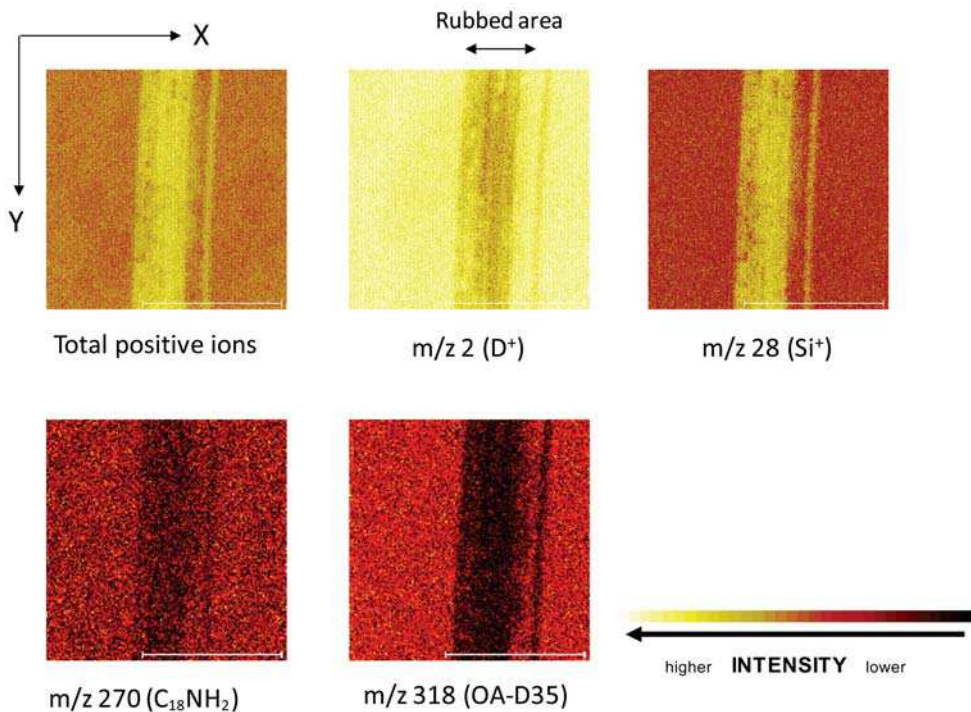Fig. 14. Friction trace of the binary-component film during the ball-on-rotating-flat test

Fig. 15. Chemical mapping of the $C_{18}NH_2$ + OA-D35 binary film after the tribo-test
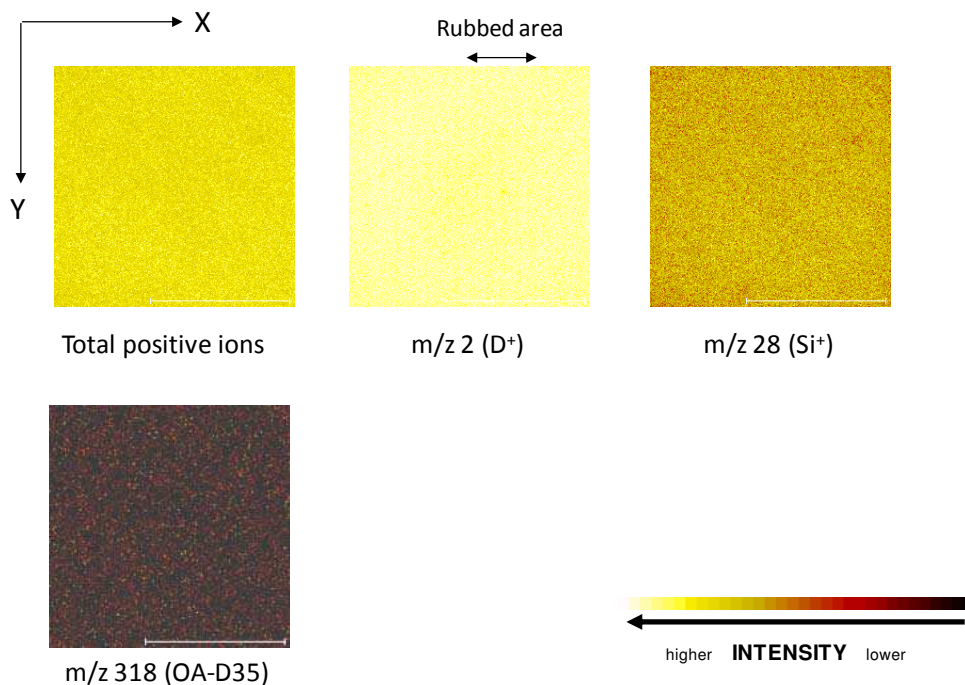
Fig. 16. Chemical mapping of the $C_{18}OH$ + OA-D35 binary film after the tribo-test

By contrast, the binary-component monomolecular film from $C_{18}OH$ + OA-D35 provided a longer lifetime with low friction. Almost no changes in chemical mapping after the tribo-test for 200 s were observed (Figure 16). The results indicate that the $C_{18}OH$ + OA-D35 binary film remained on the surface even after the tribo-test. In consequence, the tribological properties of the binary-component monomolecular film are in good agreement with the results of SIMS analysis.

An interaction between $C_{18}NH_2$ and OA-D35 through the ionic interactions is possible. This makes the adsorption force of OA-D35 on the Si surface, which retards the durability of the film. On the other hand, an interaction of $C_{18}OH$ with OA-D35 is possible through hydrogen bonding between the polar functional groups, alcohol, and carboxyl group. It should be noted that the hydrogen bond is much weaker than the ionic bond. Therefore, the adsorption force of OA-D35 was not weakened by the presence of $C_{18}OH$, which, advantageously, seems to form certain mobile phases on the surface.

2.4 Lubrication mechanism of diamond-like carbon coatings with water [17-18]

Diamond-like carbon (DLC) coatings on metallic materials possess many advantages to tribo-materials such as corrosion resistance, wear resistance, and friction reduction [19]. One of the features of using a DLC coating as a tribo-material is its applicability in humid environments or in water [20]. Furthermore, it has been reported that water improves the tribological properties of DLC. Although the formation of a boundary film by the tribo-chemical reaction of water with DLC has been suggested, a mechanistic investigation based

on surface chemistry is difficult. The tribo-chemical reaction of water is supposed to provide hydrogen or oxygen to DLC surfaces. Besides water as lubricating fluid, there are other sources of hydrogen and oxygen atoms under tribological conditions. Examples include oxygen in air or metal oxides, hydrogen in organic contaminants, or DLC itself. Resources of hydrogen or oxygen could not be identified by the usual procedure, even if increments of these elements on surfaces were detected after rubbing. The stable isotopic tracer technique is expected to be powerful tool in studying the tribo-chemistry of DLC. Heavy water, such as D_2O and $H_2^{18}O$ were employed in this work. DLC coatings were deposited on the silicon surface by a thermal electron excited chemical vapor deposition procedure using toluene as carbon source. The resultant material was slid against a SUS 440C (JIS) stainless steel ball at a load of 10 N under a reciprocating motion at the frequency of 1 Hz. The three lubricants, H_2O, D_2O, $H_2^{18}O$ provided similar tribological properties, as shown in Figure 17.
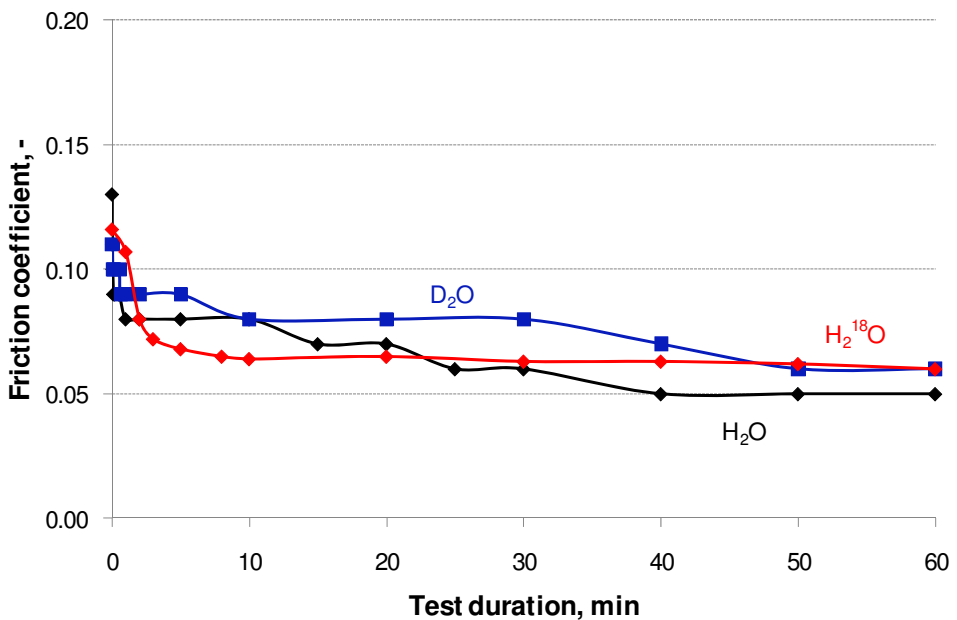

Fig. 17. Friction trace during the tribo-test with water or heavy water

Chemical mapping of the DLC surfaces obtained by SIMS analysis shows a remarkable increase in deuterium content on the rubbed surface with D_2O (Figure 18). Careful analysis of the mapping indicates the deuterium is bonded to oxygen (OD, m/z at 17) and to carbon (CD, m/z at 14). It should be noted that the fragment ion of m/z 14 could be identified as the CD moiety or CH_2 moiety. Presence of the former was supported by another considerable fragment ion of m/z 2, which corresponds to D. An increase in ^{18}O on the surfaces rubbed with $H_2^{18}O$ also supports the tribo-chemical reaction of water with DLC. A considerable increase in the fragment ions of m/z 18 and m/z 19, which corresponded to ^{18}O and ^{18}OH, respectively, indicates the formation of a new carbon-oxygen bond. It should be noted that the contents of ^{16}O (regular oxygen) outside the worn surface is higher than that inside worn surface. The results suggest that ^{16}O-containing compounds that existed on

nonrubbed surfaces were worn off under the tribological conditions. However, identification of the ^{16}O-containing compound(s) on nonrubbed surface was difficult by the SIMS analysis.

On the basis of SIMS analysis, we wish to propose the mechanism of tribo-chemical reaction of water with DLC as expressed in Figure 19. Both homolysis and heterolysis are possible as the initial step of the reaction when DLC was exposed to mechanical stress. The former yields carbon radicals and the latter yields carbocations and carbanions as active intermediates. Then heavy water reacts with the active intermediates and results in the formation of new C–D and C–OD bonds. In summary, clear evidence of the tribo-chemical reaction of water with DLC was observed using two isotopic tracers, deuterium and [18]O.

2.5 Lubrication mechanism of organic friction modifier additives in hydrocarbon oils [21]

GMO (Glycerol monooleate, 2,3-dihydroxypropyl 9(Z)-octadecenoate) is known as one of the organic friction modifiers that improves the tribological properties of hydrocarbon oils. In fact, a solution of GMO in PAO (poly-alpha-olefin) dramatically reduced the friction of steel-DLC [22]. An XPS analysis of the rubbed surface with GMO-PAO indicated the presence of carbonyl compounds on the surface [23]. The results suggest that adsorption of GMO yielded the boundary film on the surface, thereby improving the tribological properties. However, the chemical resolution of XPS analysis for carbon is not sufficient for further investigations. There are two possibilities for the structure of the boundary film. One is an adsorption film of GMO itself and the other is an adsorption film of oleic acid, which is produced by the decomposition of GMO under the tribological conditions. It is difficult to distinguish between GMO and carboxylic acid by their chemical shifts of the carbonyl group.
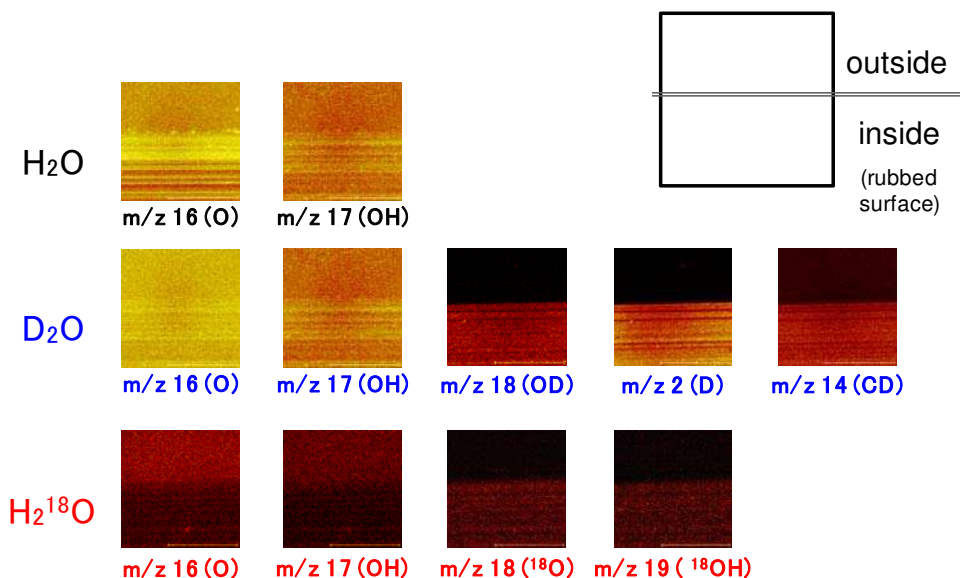

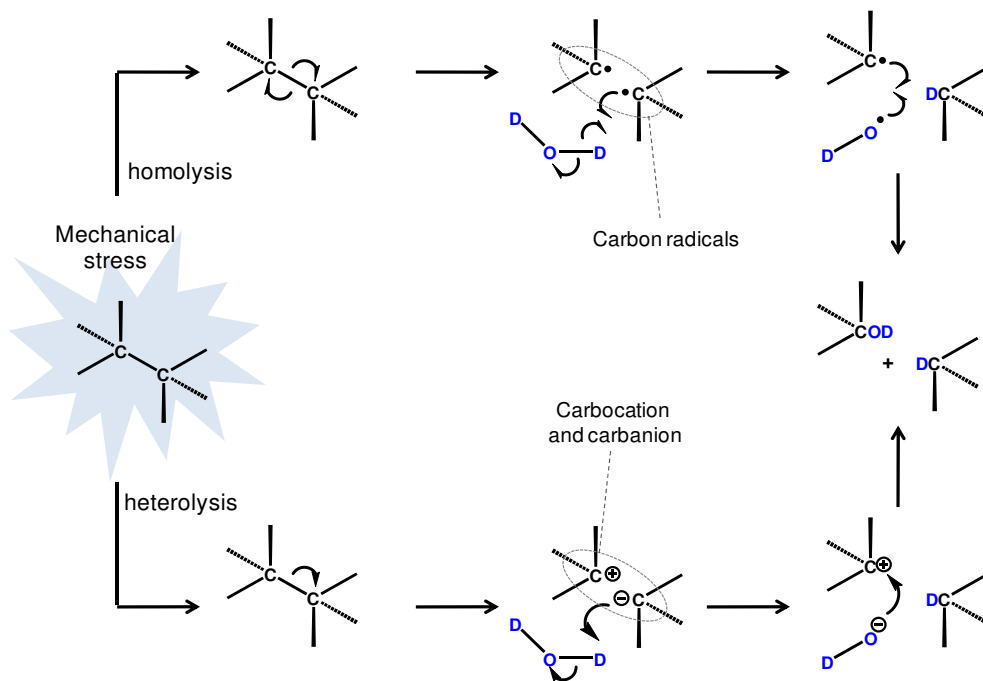Fig. 18. Chemical mapping of DLC surface after tribo-test with water

Fig. 19. Reaction mechanism of water with DLC surface under the tribological conditions

There are other ways in which carbonyl compounds are produced on the rubbed surface. An auto-oxidation of hydrocarbons usually occurs during the tribo-test under air. The reaction yields various organic oxides including carbonyl compounds. More troublesome, organic contaminants including carbonyl compounds exist everywhere. Therefore, it is difficult to eliminate carbonyl compounds derived not from GMO, but from sources other than GMO. The present stable isotopic tracer technique would clarify all of these problems. For this purpose, perdeuterio-GMO (in which all hydrogen atoms in GMO are substituted with deuterium) was desired. However, preparation of perdeuterio-GMO seemed difficult because of the availability of its precursors. Generally, GMO is prepared by the esterification of 9(Z)-octadecenoic acid (oleic acid) with propane-1,2,3-triol (glycerol). Commercially available precursors for isotope labeled GMO (where at least one atom is substituted by D or ^{13}C) are listed in Figure 20. Due to limitations in the available precursors, we were required to design isotopic labeled GMO that makes SIMS analysis effective. For this purpose, the fragmentation of GMO in SIMS analysis was considered carefully. GMO has two moieties: an alcoholic moiety with three carbons and the carbonyl moiety with 18 carbons. One of the major fragmentations of GMO is the scission of the ester bond, dividing GMO into a three-carbon moiety and 18-carbon moiety. To identify both fragments as fingerprint fragments in SIMS analysis, we have selected two precursors. One is tri-^{13}C-propane-1,2,3-triol and the other is 1-[13]C-9(Z)-octadecenoic acid. It should be noted that the former produces the three-carbon fragment with increments of m/z 3 from the natural (unlabeled) propane-1,2,3-triol. The latter produces the 18-carbon fragment with increments of m/z 1 from the natural 9(Z)-octadecenoic acid. In this manner two labeled-GMOs, namely c-GMO and g-GMO, were prepared (Figure 21).

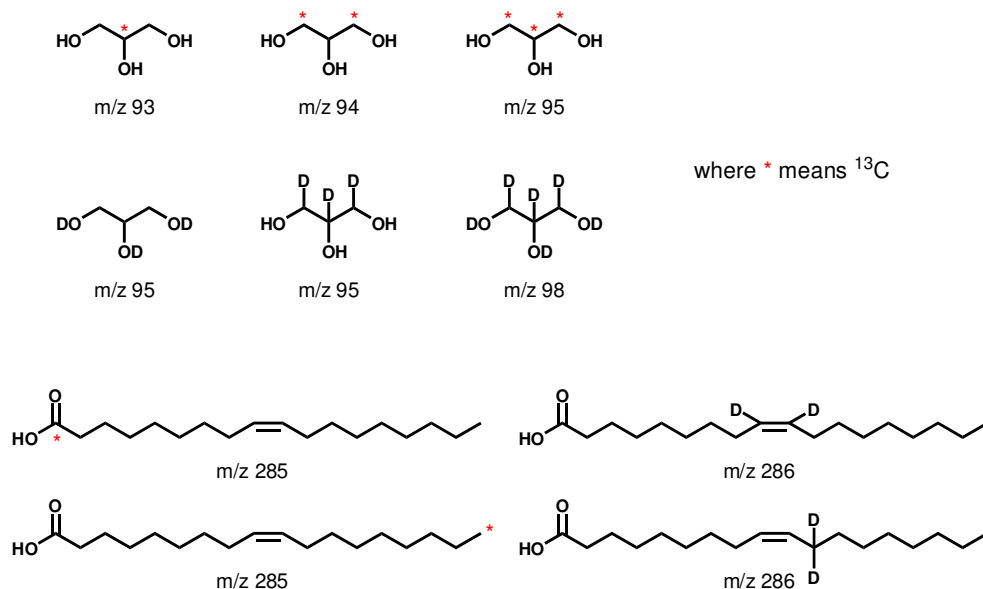m/z 93   m/z 94   m/z 95

where * means ^{13}C

m/z 95   m/z 95   m/z 98

m/z 285   m/z 286

m/z 285   m/z 286

Fig. 20. List of commercially available 9(Z)-octadecenoic acid and propane-1,2,3-triol labeled with stable isotope(s)

GMO m = 356

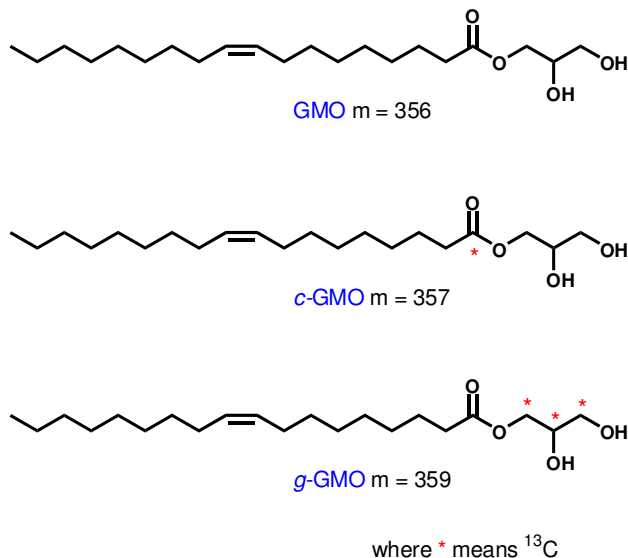c-GMO m = 357

g-GMO m = 359

where * means ^{13}C

Fig. 21. Structure of labeled GMO as a model additive

We acquired mass spectra of GMOs on nonrubbed surfaces to find out their "fingerprint" fragment ions. GMO yielded fragment ions at m/z 265 and 339 in positive ion spectra and at m/z 280 in negative ion spectra. c-GMO and g-GMO gave fragment ions according to their number of ^{13}C. These fragment ions were generated by scission of the carbon-oxygen bond

in the additive molecule. Here we paid attention to the following fragments of GMO to investigate the boundary film formed on the rubbed surfaces (Figure 22).

"Fragment-A" as the acyl moiety

"Fragment-C" as the carboxyl moiety

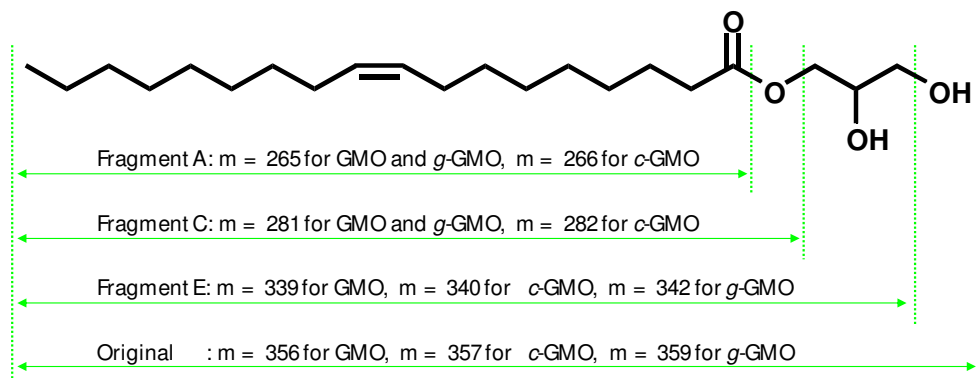"Fragment-E" as an ester dehydroxylated from the original molecule

Fragment A: m = 265 for GMO and *g*-GMO, m = 266 for *c*-GMO

Fragment C: m = 281 for GMO and *g*-GMO, m = 282 for *c*-GMO

Fragment E: m = 339 for GMO, m = 340 for *c*-GMO, m = 342 for *g*-GMO

Original   : m = 356 for GMO, m = 357 for *c*-GMO, m = 359 for *g*-GMO

Fig. 22. Formula weight of the fragment ions from GMOs

2.6 SIMS analysis of GMO on DLC

Three GMOs were dissolved in PAO and the solutions were employed for the tribo-test. All GMOs provided similar tribological properties, as shown in Figure 23. The results indicate there are no effects on isotope(s) on the tribological properties, which is essential in the use of an isotope-labeled molecule for chemical analysis.
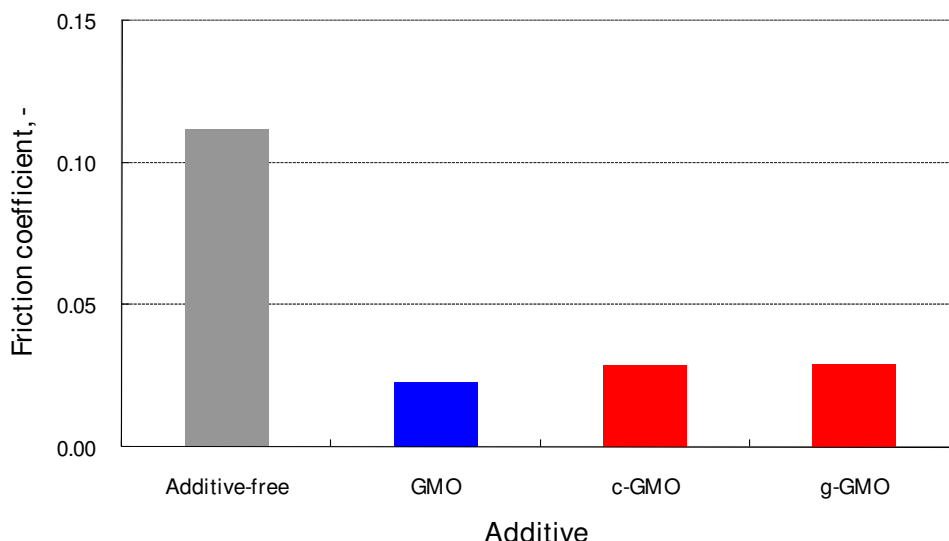

Fig. 23. Results of the tribo-test using labeled GMO in PAO

"Fragment-A" and "Fragment-E" were found in the positive mass spectra, and "Fragment-C" was found in the negative mass spectra of the rubbed surfaces (Figures 24-25). The hydrolysis of GMO yields 9Z-octadecenoic acid (oleic acid), which may adsorb on DLC surfaces. We confirmed analytically whether or not the acid exists on the surfaces. GMO and 9Z-octadecenoic acid afford "Fragment-A" and "Fragment-C." Obviously, "Fragment-E" is attributed to GMO. We compared the relative intensity of (Fragment-A)/(Fragment-E). Our hypothesis is as follows; if the relative intensity of the acid on the wear track is higher than that on the nonrubbed surface, then the acid exists on the rubbed surface. We found the same relative intensities of the fragments. Therefore, the boundary film is mainly composed of GMO as an ester, and if at all, adsorption from the acid constitutes a minor portion. These results indicate that hydroxyl group in GMO is an anchor for interactions with the DLC surfaces.

Finally, we wish to propose the contents of the boundary film that provide low friction upon steel-DLC contact. Adsorption of GMO on the rubbed and on the nonrubbed DLC was detected by SIMS analysis. It has been reported that rubbing can activate DLC surfaces, which result in the adsorption of additives [24, 20]. However, we could not find any clear
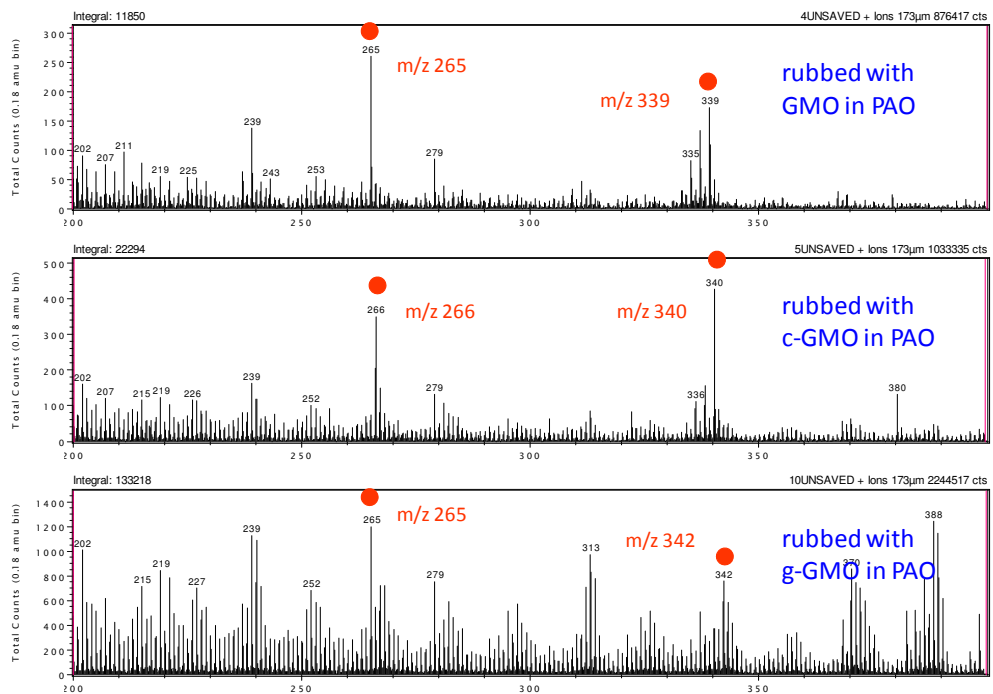

Fig. 24. Mass spectrum of wear track rubbed with GMOs (m/z 200–400, positive)
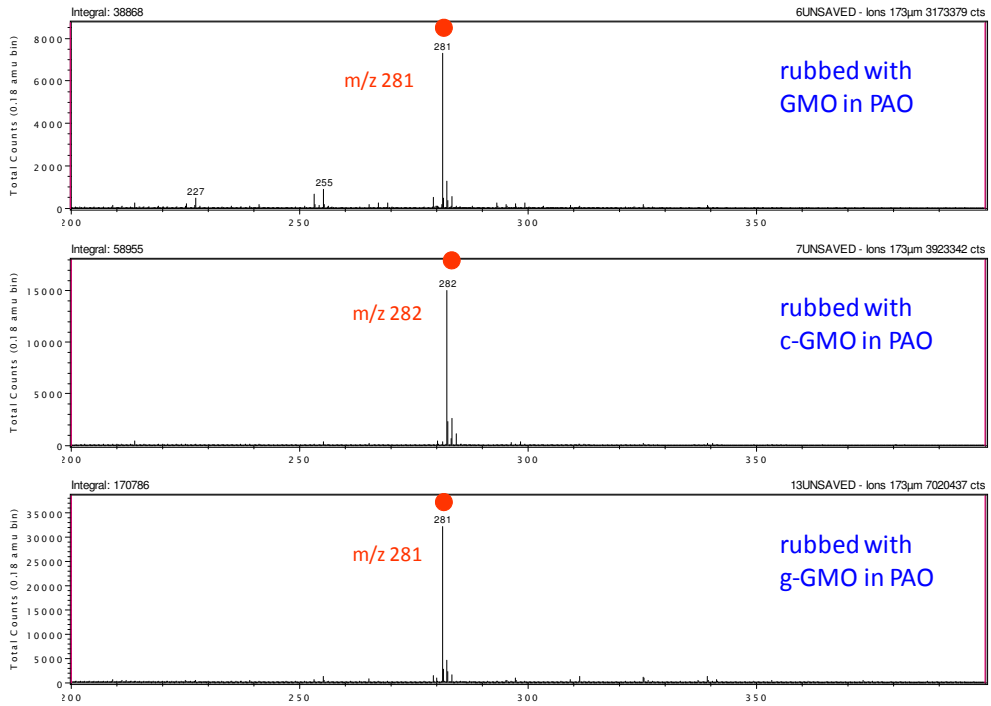
Fig. 25. Mass spectrum of wear track rubbed with GMOs (m/z 200–400, negative)

evidence for the activation of surfaces by rubbing, if the intensities of GMO on the rubbed surfaces were compared with those on the nonrubbed surfaces. Aside from "Fragment-A" and "Fragment E," several broad peaks were found in the mass spectrum. Careful analysis of the spectrum revealed that the cycle of the broad peaks is approximately m/z 14, indicating a methylene (CH_2, m/z 14) unit exists on DLC surfaces. The fragment ions are likely attributed to PAO, which is the major component of the system. A liquid clathrate-type boundary film (which involves an insertion of a branched hydrocarbon moiety in PAO into the adsorption film of GMO) was suggested [21].

3. Scope and limitations

In this article, we introduced a new technique for the investigation of tribo-chemistry that is based on stable isotopic tracers. The potential applicability of this technique would include the following three categories.

1. Degradation of preformed boundary film: Examples include monomolecular film; self-assembled mono-layers (SAMs); and any other surface treatment, including coatings.

For this purpose, isotope-labeled compounds can be employed as precursors of surface treatment.

2. The interaction of additives on the rubbed surface: The results of the binary-component monomolecular film can be applied to study synergism or antagonism for each additive in multicomponent lubricants.

3. Tribo-chemical reaction of base fluids with the surfaces of materials: Simple chemicals in the chemical structure, such as water, are applicable for this purpose at present. The main difficulties lie in availability of isotope-labeled base fluids.

4. The interaction of additive molecules with tribological surfaces: This is still an emerging technique for tracing the target molecule (usually tribo-improving additive) after the tribological process. The most challenging aspect of this technique is to detect small quantities of isotope(s) present in the system. For example, the solution of c-GMO in PAO contains approximately 0.04% of the labeled ^{13}C compared to the total number of carbons in the solution. Note that ^{13}C yields a fragment ion of m/z 13, which is the same m/z as ^{12}CH from hydrocarbons. If a considerable amount of ^{13}C exists in the system, the intensity of the fragment ion at m/z 13 should be obviously increased. The detection of these small quantities of isotopes is difficult. We have solved this problem by tracing major fragment ions derived from two or three precursors. This requires well designed model molecules based on the fragmentation of molecules during SIMS analysis. The introduction of the stable isotope(s) into the appropriate position in the molecule is essential.

It should be pointed out that the stable isotopic technique is highly suitable for organic compounds comprised of only hydrogen and carbon, and possibly also those containing oxygen and/or nitrogen atoms. For these organic compounds, the conventional surface analyses for tribology such as AES, EPMA, and XPS do not provide sufficient chemical resolution. Therefore, it is usually difficult to distinguish between the target molecule and organic contaminants. Usually there are small quantities of the target molecule on the rubbed surface. This makes the surface analysis more difficult. On the other hand, most tribo-active elements in lubricants, such as phosphorus, sulfur, molybdenum, zinc, and chlorine are well identified by the conventional surface analyses in tribology. Although AES, EPMA, and XPS can well detect the heavy elements with high sensitivity, they do not or hardly detect the light elements such as hydrogen and carbon. SIMS detects all elements if they are effectively ionized.

SIMS is a surface sensitive analysis whose analytical depth is as thin as 1–2 nm. Therefore, the sample should contain smooth surfaces to obtain optimal analytical results. The tribological process usually results in surfaces with submicrometer asperities even under a mild wear regime. The present work was achieved by employing wear resistance materials such as DLC. SIMS analysis was performed before wear occurs. This implies the technique is limited to mixed lubrication under low wear conditions. The placement of D, ^{13}C, or ^{18}O enriched atoms at the appropriate position(s) in the molecule is not always available at a reasonable cost. Therefore, isotope-labeled molecule should be designed based on their fragmentation during SIMS analysis.

SIMS approaches in tribo-chemistry using nonlabeled additives have been also achieved by detecting molecular ions or quasi-molecular ions [25-29]. However, signals corresponding to

the target molecule are weak. Our isotope labeled approach usually provides clear signals with detailed analysis of the boundary film. In addition to these advantages of SIMS, the combination of multiple analytical tools is highly recommended for studying tribo-chemistry [30-31].

4. References

[1] Pawlak, Z. (2003): Tribochemistry of Lubricating Oils. Elsevier B.V., Amsterdam.

[2] Allum, K.G.; Forbes, E.S. (1968): The Load-carrying Mechanism of Organic Sulphur Compounds. Application of Electron Probe Microanalysis . ASLE Transactions 11 2: 162-175.

[3] Buckley, D.H.; Pepper, St.V. (1972): Elemental Analysis of a Friction and Wear Surface During Sliding Using Auger Spectroscopy . ASLE Transactions 15 4: 252-260.

[4] Moulder, J.F.; Stickle, W.F.; Sobol, P.F.; Bomben, K.D. (1995): Handbook of X-Ray Photoelectron Spectroscopy. Edited by Chastain, J.; King, R.C.Jr. ULVAC-PHI, Inc., Chigasaki, Japan.

[5] Kasrai, M.; Cutler, J.N.; Gore, K.; Canning, G.; Bancroft, G.M.; Tan, K.H. (1998): The Chemistry of Antiwear Films Generated by the Combination of ZDP and MoDTC Examined by X-ray Absorption Spectroscopy. Tribology Transactions 41 1: 69-77.

[6] Benninghoven, A.; Hagenhoff, B.; Niehuis E. (1993): Surface MS: probing real-world samples. Analytical Chemistry 65 14: 630-640.

[7] Vickerman, J.C.; Gilmore, I.S. Surface Analysis - The Principal Techniques, 2nd Edition (2009): John Wiley and Sons, West Sussex.

[8] Criss, R.E. (1999): Principles of Stable Isotope Distribution. Oxford University Press, New York.

[9] Sakurai, T.; Ikeda, S.; Okabe, H. (1962): The Mechanism of Reaction of Sulfur Compounds with Steel Surface During Boundary Lubrication, Using S35 as a Tracer. ASLE Transactions 5 1: 67-74.

[10] Vickerman, J.C.; Briggs, D; Henderson, A. (2007): Static SIMS Library, 4th edition. SurfaceSpectra Ltd. Manchester.

[11] Minami, I.; Kubo, T.; Fujiwara, S.; Ogasawara, Y.; Nanao, H.; Mori, S. (2005): Investigation of tribo-chemistry by means of stable isotopic tracers; TOF-SIMS analysis of Langmuir-Blodgett films and examination of their tribological properties. Tribology Letters 20 3/4: 287-297.

[12] Bowden, F. P.; Tabor, D. (2001): The Friction and Lubrication of Solids. Oxford University Press, New York.

[13] Novotny, V.; Swalen, J.D.; Rabe, J.P. (1989): Tribology of Langmuir-Blodgett Layers. Langmuir 5 2: 485-489.

[14] Nutting, G.C., Harkins, W.D. (1939): Pressure-Area relations of Fatty Acid and Alcohol Monolayers. Journal of American Chemical Society 61 : 1180-1187.

[15] Minami, I.; Furesawa, T.; Kubo, T.; Nanao, H.; Mori, S. (2008): Investigation of tribo-chemistry by means of stable isotopic tracers: Mechanism for durability of monomolecular boundary film. Tribology International 41 11: 1056-1062.

[16] Dominguez, D.D.; Mowery, R.L.; Turner, N.H. (1994): Friction and Durabilities of Well-Orderd, Close-Packed Carboxylic Acid Monolayers Deposited on Glass and Steel Surfaces by the Langmurir-Blodgett Technique. Tribology Transactions 37 1: 59-66.

[17] Wu, X.; Ohana, T.; Tanaka, A.; Kubo, T.; Nanao, H.; Minami, I.; Mori, S. (2007): Tribochemical investigation of DLC coating tested against steel in water using a stable isotopic tracer. Diamond and Related Materials 16 9: 1760-1764.

[18] Wu, X.; Ohana, T.; Tanaka, A.; Kubo, T.; Nanao, H.; Minami, I.; Mori, S. (2008): Tribochemical investigation of DLC coating in water using stable isotopic tracers. Applied Surface Science 254 11: 3397-3402.

[19] Miyoshi, K.; Street, K.W.Jr. (2004): Novel carbons in tribology. Tribology International 37: 865-868.

[20] Li, H.; Xu, T.; Wang, C.; Chen, J.; Zhou, H.; Liu, H. (2005): Tribochemical effects on the friction and wear behaviors of diamond-like carbon film under high relative humidity condition. Tribology Letters 19 3: 231-238.

[21] Minami, I.; Kubo, T.; Nanao, H.; Mori, S.; Okuda, S.; Sagawa, T. (2007): Investigation of Tribo-Chemistry by Means of Stable Isotopic Tracers, Part 2: Lubrication Mechanism of Friction Modifiers on Diamond-Like Carbon. Tribology Transactions 50 4: 477-487.

[22] Kano, M. (2006): Super low friction of DLC applied to engine cam follower lubricated with ester-containing oil. Tribology International 39: 1682-1685.

[23] Ye, J.; Okamoto, Y.; Yasuda, Y. (2008): Direct Insight into Near-frictionless Behavior Displayed by Diamond-like Carbon Coatings in Lubricants. Tribology Letters 29 1: 53-56.

[24] Kano, M.; Yasuda, Y.; Okamoto, Y.; Mabuchi, Y.; Hamada, T.; Ueno, T.; Ye, J.; Konishi, S.; Takeshima, S.; Martin, J.M.; Bouchet, M.I. De Barros; Le Mogne, T. (2005): Ultralow friction of DLC in presence of glycerol mono-oleate (GMO). Tribology Letters 18 2: 245-251.

[25] Dauchot, G.; Castro, E. De; Repoux, M.; Combarieu, R.; Montmitonnet, P.; Delamare, F. (2006): Application of ToF-SIMS surface analysis to tribochemistry in metal forming processes. Wear 260: 296-304.

[26] Wiltord, F.; Martin, J.M.; Le Mogne, T.; Jarnias, F.; Querry, M.; Vergne, P. (2006): Reaction mechanisms of alcohols on aluminum surfaces. Tribologia 37 6: 7-20.

[27] Tohyama, M.; Ohmori, T.; Murase, A. Masuko, M. (2009): Friction reducing effect of multiply adsorptive organic polymer. Tribology International 42 6: 926-933.

[28] Gunsta, U.; Zabelb, W. R.; Vallec, N.; Migeonc, H.-N.; Pollb, G.; Arlinghausa, H.F. (2010): Investigation of laminated fabric cages used in rolling bearings by ToF-SIMS. Tribology International 43 5-6: 1005-1011.

[29] Reichelt, M.; Gunst, U.; Wolf, T.; Mayer, J.; Arlinghaus, H.F.; Gold, P.W. (2010): Nanoindentation, TEM and ToF-SIMS studies of the tribological layer system of cylindrical roller thrust bearings lubricated with different oil additive formulations. Wear 268 11-12: 1205-1213.

[30] Georges, J.M.; Martin, J.M.; Mathia, T.; Kapsa, P.H.; Meille, G.; Montes, H. (1979): Mechanism of boundary lubrication with zinc dithiophosphate. Wear 53 1: 9-34.

[31] Minfray, C.; Martin, J.M.; Esnouf, C.; Le Mogne, T.; Kersting, R.; Hagenhoff, B. (2004): A multi-technique approach of tribofilm characterization. Thin Solid Films 447-448: 272-277.
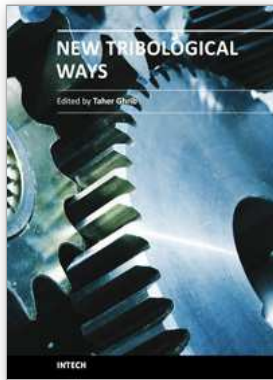
New Tribological Ways

Edited by Dr. Taher Ghrib

This book aims to recapitulate old information's available and brings new information's that are with the fashion research on an atomic and nanometric scale in various fields by introducing several mathematical models to measure some parameters characterizing metals like the hydrodynamic elasticity coefficient, hardness, lubricant viscosity, viscosity coefficient, tensile strength .... It uses new measurement techniques very developed and nondestructive. Its principal distinctions of the other books, that it brings practical manners to model and to optimize the cutting process using various parameters and different techniques, namely, using water of high-velocity stream, tool with different form and radius, the cutting temperature effect, that can be measured with sufficient accuracy not only at a research lab and also with a theoretical forecast. This book aspire to minimize and eliminate the losses resulting from surfaces friction and wear which leads to a greater machining efficiency and to a better execution, fewer breakdowns and a significant saving. A great part is devoted to lubrication, of which the goal is to find the famous techniques using solid and liquid lubricant films applied for giving super low friction coefficients and improving the lubricant properties on surfaces.

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