

TRIBOCHEMICAL ACTIVITY OF NASCENT METAL SURFACES

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Abstract

Chemical nature of nascent metal surfaces which is one of the important active sources for tribochemical reactions was investigated using a newly developed method. Some enhanced activities were observed. For example, organic compounds chemisorbed on nascent gold surfaces and aromatic compounds decomposed on nascent nickel surfaces resulting in hydrogen evolution. Non-polar compounds such as organic sulfides had a higher chemisorption activity on nascent steel surfaces than polar compounds such as fatty acids and phosphates. Organic sulfides reacted directly with nascent steel surfaces and the surface was covered with metal sulfides. The activity for the chemisorption of organic compounds was closely dependent on the electronic structure of metals. Although benzene chemisorbed very easily on nascent surfaces of transition metals, it did not chemisorb on nascent surfaces of simple metals. Boundary lubricating behaviors of extreme pressure additives were explained on the bases of the chemical activities of nascent surfaces obtained in this investigation. Under mild conditions, polar compounds such as fatty acids and phosphates were effective for boundary lubrication, because surfaces are covered with oxide layers. On the other hand, sulfides were more effective under severe conditions where the oxide layers were removed and the nascent surfaces were formed.

1. INTRODUCTION

Tribological properties under boundary lubricating conditions are strongly affected by tribochemical surface reactions of materials with lubricant components and surrounding gases. It is difficult to understand the basic mechanism of tribochemical reactions because mechanical energy is supplied to the interface of materials and lubricants. Sometimes, tribological reactions have been reported as 'miracle' when the tribological behavior obtained could not be explained by the common knowledge in textbooks. However, the author believe that any tribochemical reactions occur under the universal rule of chemical reactions. It is necessary to make clear the basic mechanism of tribochemical reactions in order to understand basic mechanisms of boundary lubrications(1).

There are two main causes for tribochemical activation, that is, temperature and pressure rise at mechanical contacts, and enhanced activity of mechanically worked surfaces. Many papers have been reported on the enhanced active sources, such as lattice defects(2), exoelectrons(3), (4) and nascent surfaces(5)-(8). In general, metal surfaces are chemically stabilized by surface layers such as metal oxides, organic contaminants and adsorbed compounds. The surface layers are removed by tribological contacts, and fresh or nascent metal surfaces are formed. The nascent surfaces have been believed to be chemically active, because they have dangling bonds and surface defects. In this paper, tribochemical activity of nascent metal surfaces will be reviewed based on recent results obtained in our group.

Many tribologists have pointed out the important role of the nascent surfaces on tribochemical reactions. Evaporated films and clean surfaces of single crystals have been used as a model surface of the nascent surfaces. For example, Roberts et al. reported that α -olefins chemisorb on evaporated aluminum films(5), and Morecroft reported

that evaporated iron films exhibited so high activity that nonadecanoic acid decomposed on it(6). They pointed out that these activities plays an important role on surface reaction of lubricants under boundary lubricating conditions.

The chemical nature of evaporated films is similar to that of nascent surface as far as oxide-free surfaces can be obtained. However, nascent surfaces are expected to have a lot of surface defects which may enhance their chemical activity. Therefore, we have been studying on the chemical nature of nascent surfaces formed by scratching. Recent results are described in this paper.

2. EXPERIMENTAL

Several kinds of metals and alloys were used as a specimen of which size was 30 mm in diameter. Metals used were transition metals such as nickel, iron, cobalt and chromium and typical metals such as copper, silver, gold, zinc, aluminum, tin, lead. Alloys such as Ni-Al, Ni-Cu, Cu-Al, Cu-Sn and Cu-Pb were also used.

Organic compounds which have a different functional group were used as a model compounds of lubricants. A sample gas of paraffins, olefins, aromatics, alcohols, ethers, carboxylic acids, esters, sulfides and halides were introduced through a variable leak valve.

The experimental apparatus was shown in Figure 1. All experiments were carried out at room temperature in a high vacuum chamber in which a small lathe was constructed. The details of the apparatus has been reported elsewhere(9). Nascent metal surfaces were formed by scratching under the condition of 1 to 6 cm/s of scratching speed in sample

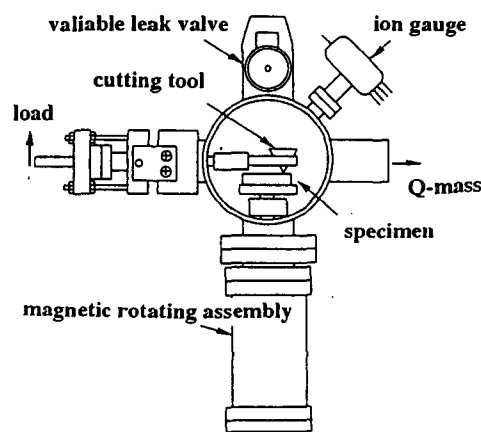


Figure 1. Experimental apparatus for estimation of nascent metal surfaces.

3. RESULTS AND DISCUSSION

3.1 Estimation of chemical activity

After the partial pressure of a sample gas became constant, specimen surface was scratched with a ceramic

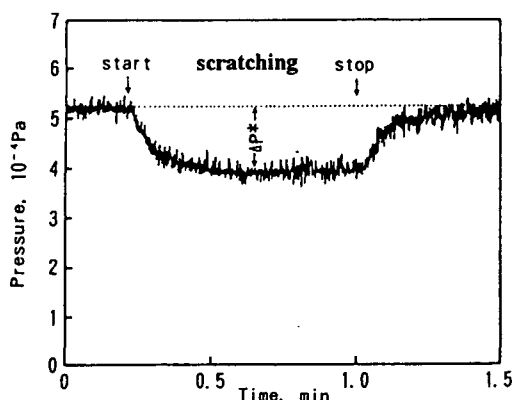


Figure 2. Pressure decrease due to chemisorption of 1-hexene on nascent gold surface.

gas atmosphere of which partial pressure was 10^4 Pa. Pressure change owing to chemisorption and surface reactions was monitored with a quadrupole mass spectrometer. In many cases, the amount of adsorption was less than monolayer estimated from the pressure decrease of sample gas due to adsorption. Adsorption activity of organic gases was estimated from the time dependence of the pressure decrease(10).tip. The partial pressure decreased exponentially owing to adsorption of the sample gas as shown in Figure 2. Since pressure decrease due to adsorption of inert gases such as argon was not observed, only chemisorption on nascent surfaces can be detected by this method. There are two main causes for the chemisorption as mentioned above, surface activity of nascent surfaces and high temperature at scratching contacts. Since molecules collide on nascent surfaces apart from the mechanical contact as shown in Figure 3, we can eliminate the thermal effect on the adsorption process. In other words, we can estimate a chemical interaction between adsorbed molecules and nascent surfaces without thermal effect.

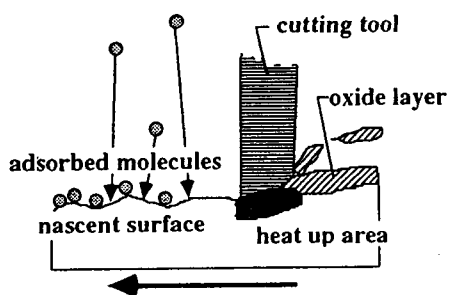


Figure 3. Adsorption model on nascent surfaces formed by scratching.

'Adsorption activity' of sample gases can be estimated from the time dependence of pressure decrease during adsorption. A good semi-logarithmic relation of the pressure decrease was obtained. Since the slope of the relation is proportional to sticking coefficient, we can estimate 'adsorption activity' from the slope(10). The chemical nature of nascent metal surfaces will be discussed from the

'adsorption activity' hereafter.

Some part of chemisorbed compounds decomposed on the nascent surfaces and hydrogen evolution was observed in many cases. For example, it was found that catalytic decomposition of aromatic compounds was observed on nascent nickel surfaces even at room temperature(11). Decomposition of other organic compounds was also observed. Organic sulfides reacted directly with nascent steel surfaces and metal sulfides were formed on the surface. It can be concluded that nascent metal surfaces have a high reactivity.

In the following sections, the chemical nature of nascent metal surfaces will be discussed from chemisorption activity of organic compounds on the surface.

3. 2Transition metals

Adsorption activities of organic compounds on nascent steel surfaces are summarized in Table 1. The values are a relative activity on the bases of the adsorption activity of oxygen. Saturated hydrocarbons which have no functional group had no chemisorption activity even on nascent surfaces. Non-polar compounds such as olefins, benzene and organic sulfides showed a high activity for chemisorption. On the other hand, polar compounds such as fatty acid, amine and phosphate showed very low activity. These results can be explained by the Pearson's Hard and Soft Acids and Bases Principle. The non-polar compounds are classified soft bases and interact more strongly with soft acids such as metallic surfaces rather than hard acids, that is, metal oxides. The most important result obtained here is that fatty acids are known as a good oiliness agent because they chemisorb on oxide covered metal surfaces, but they do not interact with nascent steel surfaces compared to the soft compounds.

Table 1. Adsorption activity of model compounds of lubricants on nascent steel surfaces.

| model compounds | relative activity |
|---------------------|-------------------|
| base oil | |
| n-hexane | 0 |
| cyclohexane | 0 |
| 1-hexene | 0.22 |
| cyclohexene | 0.63 |
| benzene | 0.79 |
| additive | |
| diethyl disulfides | 0.22 |
| trimethyl phosphate | 0.01 |
| propyl amine | 0.01 |
| propionic acid | 0.01 |
| methyl propionate | 0.17 |
| atmosphere | |
| nitrogen | 0 |
| oxygen | 1.00 |
| water | 0.07 |

Chemisorption activity of ethers and alcohols were closely dependent on their molecular structures. Figure 4 shows the effect of the electron releasing ability of alkyl group on chemisorption activity on nascent nickel surfaces. It is obvious that the higher the electron releasing ability,

the higher the chemisorption activity. These results indicate that alcohols and ethers chemisorb through the donation of lone pair electrons to nascent metal surfaces.

Figure 5 shows chemisorption activity of butyl sulfides on nascent transition metal surfaces which are a model compounds of *e. p.* additives. The activity was closely dependent on the electron releasing ability of butyl group.

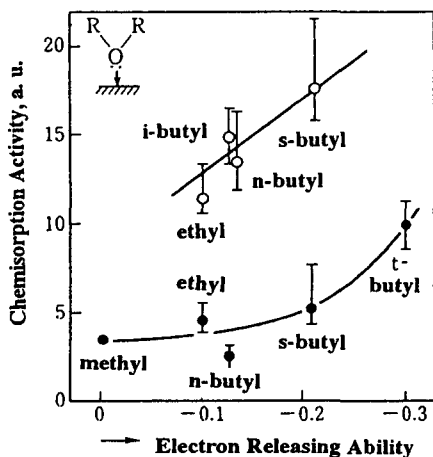


Figure 4. Chemisorption activity of alcohols and ethers on nascent nickel surface.

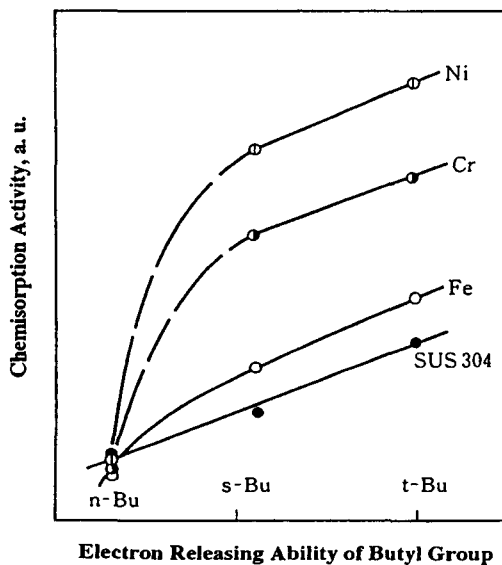


Figure 5. Chemisorption activity of butyl sulfides on nascent surfaces of transition metals.

The relation with the sulfides is much clearer than that obtained with ethers shown in Figure 4. Butyl sulfide molecules also chemisorbed through the donation of lone pair electrons to nascent metal surfaces. The adsorption activity was closely dependent on the electron releasing ability of the alkyl groups as well as the kind of metals. It may be concluded that the chemical interaction between

Chemisorption Activity, a. u.

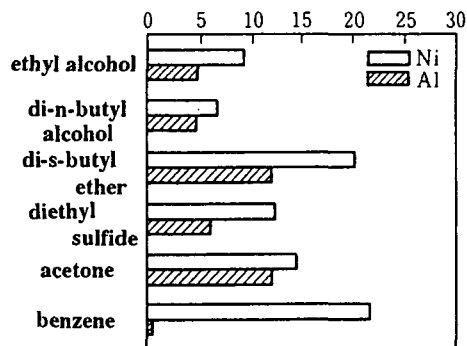


Figure 6. Comparison of chemical activities of nickel and aluminum.

the adsorbed molecules and metal surfaces is controlled by the electronic structures of sulfides and metals.

3.3 Simple metals

It was found that the chemical nature of nascent surfaces of simple metals was quite different from transition metals for the chemisorption activity of organic compounds. The chemisorption activity on the nascent aluminum surface is compared with that on nickel surface as shown in Figure 6. Nascent aluminum surfaces had no activity for benzene adsorption, but showed high activity for chemisorption of oxygen containing compounds such as ethers and ketone. Figure 7 shows a good relation of the chemisorption activity in the periodic table. Softer compounds exhibited a higher activity. Other results are summarized in Table 2. Organic compounds containing oxygen such as alcohols have a high chemisorption activity on the nascent surfaces of simple metals. However, benzene and 1-hexene did not chemisorb on the nascent surfaces of 11- to 14-group metals except for copper and gold. It is well-known that aromatic compounds and olefins chemisorb on transition metals through donation of their π -electrons to *d*-orbitals of

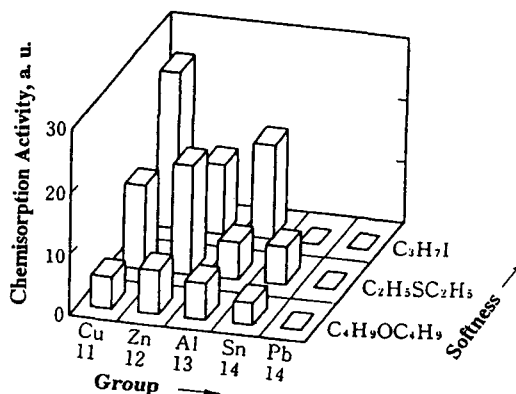


Figure 7. Chemisorption activity of some organic compounds on nascent surfaces of simple metals.

Table 2. Adsorption properties on nascent surfaces of 11 to 14-group metals.

○ : chemisorbed, △ : slightly chemisorbed,
 □ : chemisorbed only under severe conditions,
 × : chemisorption was not observed., - : no experiment.

| period | 1 B | 2 B | 3 B | 4 B | 4 B |
|--|-----|-----|-----|-----|-----|
| gases/metals | Cu | Zn | Al | Sn | Pb |
| CH ₂ =C ₆ H ₁₀ | ○ | × | × | × | × |
| C ₆ H ₁₀ | ○ | × | × | - | × |
| C ₆ H ₆ | ○ | × | × | × | × |
| C ₄ H ₉ OH | ○ | △ | ○ | × | □ |
| C ₄ H ₉ OC ₄ H ₉ | ○ | ○ | ○ | ○ | □ |
| C ₄ H ₈ O | ○ | × | ○ | × | × |
| (C ₂ H ₅) ₂ C=O | ○ | × | ○ | × | □ |
| CH ₃ COOCH ₃ | × | × | ○ | □ | × |
| C ₂ H ₅ SC ₂ H ₅ | ○ | ○ | ○ | ○ | × |
| C ₃ H ₇ I | ○ | ○ | ○ | □ | × |

transition metals. Since simple metals have no *d*-orbitals, it can be explained that they did not have the activity for the chemisorption of aromatics and olefins.

A very interesting result obtained here is a chemical activity of the nascent gold surface which exhibited a chemical activity for chemisorption as shown in Figure 2(12). Although gold is recognized as a chemically inert metal, it became active by scratching. Organic compounds except for saturated hydrocarbons chemisorbed on nascent gold surfaces, and a part of chemisorbed compounds decomposed resulting in hydrogen evolution. It is important that even aromatics and olefins chemisorbed on the nascent gold surface, although gold has no *d*-orbital. The same result was obtained on nascent copper surfaces. Since gold and copper is classified into the 11-group metal on the periodic table, they have no *d*-orbital essentially. They obtained the chemical activity like transition metals by scratching. One of the explanation for the activity is surface defects formed by scratching, of which electronic structure becomes like transition metals and there is an empty of *d*-orbitals. There is no surface analytical tool to reveal the electronic structure of scratched nascent surfaces. In other words, our method describing in this paper is a unique method to be able to estimate the chemical activity of nascent metal surfaces.

3.4 Alloys

Alloys have been used increasingly as tribomaterials in industries. As mentioned above, the chemical nature of nascent surfaces is dependent on the group of the metals, that is, transition metals and simple metals. The effect of mixing of metals on chemical nature of nascent surfaces was investigated.

Although benzene and 1-hexene which have π -electrons chemisorbed on nascent copper surfaces, the activity diminished by the addition of small amount of aluminum to copper as shown in Figure 8. There are two reasons for the deactivation of nascent copper-aluminum surface, physical and chemical effect of aluminum. The former is that the scratched surface is entirely covered with aluminum layer and chemical nature of aluminum appeared.

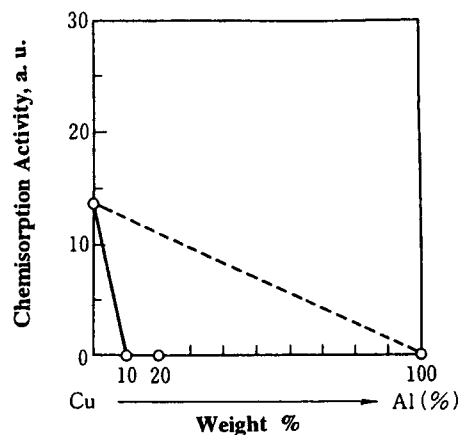


Figure 8. Additive effect of aluminum on the activity of nascent copper surface.

The latter is that chemical interaction between copper and aluminum occurs in the alloy. XPS measurements revealed that aluminum was concentrated at the scratched surface but more than ten percent of copper covered on the surface. Therefore, the scratched surface of Cu-Al alloy may be deactivated by the chemical effect of aluminum. A similar deactivation was observed on the nascent surfaces of Cu-Sn alloy and Al-Pb alloy.

Figures 9 and 10 show the chemisorption activity of nascent surfaces of Ni-Cu, Cu-Al and Al-Ni alloys as well as pure metals. The activity is indicated by the radius of the figure. Three axes indicate pure metals, and the

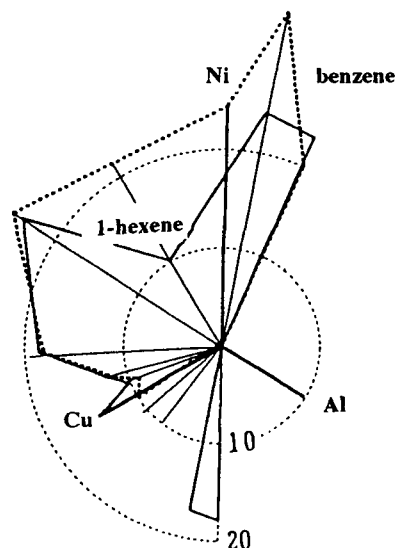


Figure 9. Chemisorption activity of benzene and 1-hexene on nascent alloy surfaces. Three axes indicate pure metals. The radius indicates the chemisorption

components between the axes mean three types of alloy. Unsaturated hydrocarbons easily chemisorbed on the nascent surfaces of nickel, copper and their alloys. On the other hand, organic compounds containing oxygen have higher activity onto the nascent surfaces of aluminum and its alloy rather than nickel.

3.5 Is it useful for understanding boundary lubrication?

These results mentioned above were obtained under high vacuum conditions. Real surface reactions in boundary lubrication occur under the effect of air, especially oxygen.

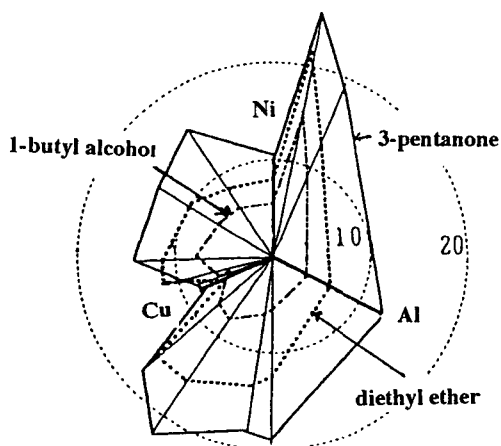


Figure 10. Chemisorption activity of alcohol, ether and ketone on nascent alloy surfaces. Three axes indicate pure metals. The radius indicates the chemisorption activity.

What is the difference between high vacuum and atmospheric pressure conditions? Under atmospheric pressure oxygen attacks metallic surfaces and the surface is covered with oxide layers within microseconds. When nascent surfaces are formed in lubricants, the surface will be attacked by the components of the lubricant, for example, oil additives as well as oxygen. Oxygen and additive molecules attack onto nascent metal surfaces competitively. The surface composition after chemisorption is dependent on the concentration of the components in lubricants as well as the reactivity of components. The concentration of oxygen in a lubricant saturated with oxygen is 10^{-2} mol/l at most which is one or two orders lower than that of additives. Therefore, it is possible that additive molecules directly attack onto nascent metal surfaces instead of oxidized surface even under atmospheric pressure, and then a part of nascent surface is covered with additive molecules. Therefore, the results obtained here are meaningful for investigation of the tribochemical surface reactions of lubricants in boundary lubrication conditions, although they were obtained under high vacuum conditions. Consequently, it is expected that the chemical activities of nascent surfaces may play an important role on boundary lubrication. Some examples is described below.

Since nascent surfaces are formed under severe conditions, their role must become important in the action mechanism of extreme pressure additives. There are two types of e. p. additives, organic sulfides and phosphates, and their activities against nascent steel surfaces were very

different as shown in Table 1. Since sulfides have a higher activity against nascent steel surfaces than phosphates, it is expected that sulfides are more effective than phosphates under severe conditions where nascent surfaces are formed.

Sakurai et al. have reported the effectiveness of phosphates and sulfides using a four-ball tester(13). Phosphates were effective under the condition of low load(a mild condition), but sulfides were more effective at a higher load(a severe condition). This result may be explained by the reactivity of the e. p. additives on material surface as the following manner. Under the mild condition, the specimen was covered with oxide layers on which polar compounds such as phosphates easily chemisorb through a polar-polar interaction, whereas sulfides reacted directly with nascent surfaces formed under the severe condition. Thus, the effectiveness of the e. p. additives can be explained by their reactivity. Ghose et al. also reported that tricresyl phosphate (TCP) was not effective under dry nitrogen, but effective under air(14). This means that TCP chemisorbed on oxide-covered surface resulting in the formation of e. p. film.

Owens et al. have pointed out the importance of chemisorption of α -olefin on its boundary lubricating performance for metal working of aluminum. They observed the chemisorption of α -olefin on an evaporated aluminum film as a model surface of nascent surfaces. However, we did not observe the chemisorption of α -olefin on nascent aluminum surface as shown Table 2. If chemisorbed layers act as a boundary lubricating film, the organic compounds containing oxygen should be more effective than α -olefin because chemisorption activity of alcohols and ethers was much higher than α -olefin. Therefore, the reason for the good lubricating performance of α -olefin for metal working of aluminum is not owing to its chemisorption activity but to some tribochemical reactions occurred at mechanical

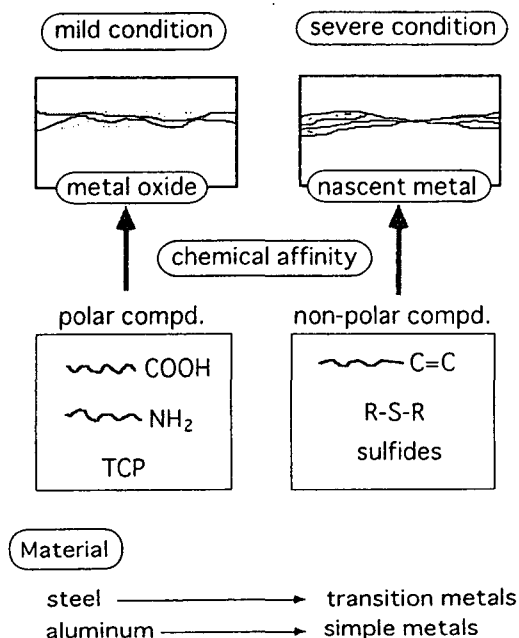


Figure 11. Tribological conditions and surface chemistry in boundary lubrication.

contacts. Recently, we have found that polymeric products were formed from 1-decene during FALEX tests of aluminum alloy in the olefin(15). The polymeric matter may act as a lubricant film. In this case, our results described in this paper have made clear the lubricating mechanism of α -olefin for metal working of aluminum and its alloy.

Tribological behavior in boundary lubrications is strongly affected by surface reactions as well as chemisorption of additives at mechanical contacts. The reactivity of additives with surfaces cannot be determined absolutely from the structure of additives, but it is a relative problem of an additive and a surface. In this paper, it is revealed that chemical nature of nascent metal surfaces was very different from that of oxide-covered surfaces. Non-polar compounds chemisorbed on metallic surfaces more easily than oxide surface, whereas polar compounds chemisorbed easily on metal oxide surfaces. Metal surfaces are covered with metal oxide layer which is removed by mechanical contacts under severe conditions. Therefore, chemical nature of metal surfaces is closely dependent on the lubricating conditions, that is, oxide surfaces under mild conditions and metallic surfaces under severe conditions. Consequently, the additives to be effective for mild conditions should be polar compounds such as fatty acids and phosphates and the effective additives under severe conditions should be non-polar compounds such as organic sulfides(Figure 11). One more important point to select a good additive is the chemical nature of metals, transition metal or simple metal.

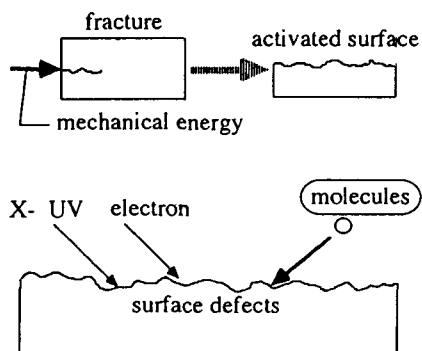


Figure 12. Dynamic characterization of tribosurfaces.

There are many surface analytical tools for characterization of solid surfaces. Surface structures, compositions and chemical bondings are analyzed by the elastic or inelastic scattering of incident particles such as photons, electrons, ions and molecules(Figure 12). However, it is very difficult to characterize tribosurfaces, because the surface structure is essentially unstable. Our method described here is unique for the chemical characterization of tribosurface.

4. CONCLUSIONS

Chemical nature of nascent metal surfaces were characterized from the chemisorption activity of organic compounds using a newly developed method.

- 1) Enhanced activities were observed on the nascent surfaces. By scratching, gold surface became so active that organic compounds chemisorbed on it.

Decomposition of other organic compounds and hydrogen evolution were also observed during scratching.

- 2) Aromatic compounds decomposed catalytically on nascent transition metal surfaces even at room temperature.
- 3) Soft compounds such as sulfides have higher activity on nascent steel surfaces than hard compounds such as fatty acids.
- 4) The chemical nature of nascent surfaces of simple metals was different from that of transition metals. According to the chemisorption activity of organic compounds, the chemical activities of nascent metal surfaces were dependent on their electronic structures.
- 5) Tribological behaviors of e. p. additives in references can be explained by the results reported in this paper.

REFERENCES

- (1) S. Jahanmir, *Trans. ASME, J. Tribol.*, **109**(1987)207.
- (2) S. Kishimoto and M. Nishioka, *J. Phys. Chem.*, **76**(1972), 1907.
- (3) K. Nakayama and H. Hashimoto, *Tribol. Trans.*, **38**(1995), 541.
- (4) C. Kajdas, *Wear*, **116**(1987), 167.
- (5) L. E. St Pierre and R. S. Owens, *Nature*, **202**(1964)1204.
- (6) D. W. Morecroft, *Wear*, **18**(1977)333.
- (7) I. L. Goldblatt, *Ind. Eng. Chem., Prod. Res. Develop.*, **10**(1970)270.
- (8) S. Mori and Y. Imaizumi, *STLE Trans.*, **31**(1988)449.
- (9) S. Mori, M. Suginoia and Y. Tamai, *ASLE Trans.*, **25**(1982)261.
- (10) S. Mori, *Appl. Surface Sci.*, **27**(1987)401.
- (11) S. Mori and M. Yoshida, *STLE Trans.*, **31**(1988)128.
- (12) S. Mori and Y. Shitara, *Appl. Surface Sci.*, **78**(1994)269.
- (13) M. Tomaru, S. Hironaka and T. Sakurai, *Wear*, **41**(1977), 141.
- (14) H. M. Ghose, J. Ferrante and F. C. Honey, NASA TM 100103(1983).
- (15) M. Igari and S. Mori, *Tribologists(J. Japanese Soc. Tribol.)*, **37**(1992)605.