

Investigation of Tribochemical Reactions by Organic Sulfides on Nascent Metal Surfaces

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Under conditions of boundary lubrication, there is direct contact and surface films such as metal oxides and organic contaminants are mechanically removed by mechanical contacts. This causes to form a chemically active nascent surface. It is essential to understand the reaction between lubricant additives and the nascent metal surface. In this research, the well known organic sulfides were selected as the model compounds of extreme pressure additives (EP additives). The catalytic effect of a nascent metal surface without thermal effect was studied using cutting method with a ceramic tip and the reaction was monitored with a quadrupole mass spectrometer. The main result is that the type of alkyl group and the number of sulfur atoms in the central chain (for instance, mono-sulfide or disulfide) have a strong influence on the adsorption and reaction of the sulfide compounds.

Keywords: nascent metal surface, organic sulfide, EP additive, quadrupole mass spectrometer, chemisorption

1. Introduction

Lubricants composed of adequate additives are widely applied in friction parts of machines in order to control friction and wear. Under mild tribological conditions, oiliness agents are well known to reduce friction. When the operational conditions such as load and temperature become severe, the lubrication regime turns to boundary. Under these conditions, anti-wear and/or extreme pressure additives are effective. They react with rubbing surfaces; thereby improve the tribological conditions.

If the metal surface is covered with oxide films, polar additives prone to adsorb on the surface followed by tribochemical reaction. Anti-wear additives (AW additives) and extreme pressure additives (EP additives) are the most popular additives which control the friction and wear in boundary lubrication. It has been reported that effectiveness of EP additives was closely dependent on contact conditions¹⁾. Forbes and co-authors reported the important role of thermal reaction of EP additives on load carrying capacity under severe conditions²⁾.

When the oxide films on metal surfaces were mechanically removed, nascent metal surfaces are exposed. As the results, adhesive wear and welding are occurred. At present, this problem is resolved by the addition of additives to the lubricant oil. To date, several EP additives are applied to prevent wear and seizure of tribo-materials at the contact³⁻⁷⁾.

We have been studied the reactivity of various organic compounds on nascent metal surfaces in previous works⁸⁻¹⁰⁾. In this study, we examined the reactivity of alkyl/alkenyl

sulfides as the model compound of major EP additives. Reactions of these sulfides on nascent transition metals that are composed of alloys were traced. Here we report the effects of molecular structure of sulfides on the reactivity. Chemical properties of the metals were also taken into account.

2. Experimental

2.1. Specimens

Transition metals period IV, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and a typical metal Zn were selected for study. These metals were cleaned ultrasonically in bath of petroleum ether. The dimensions of the disc specimens were 30 mm in diameter and 10 mm in thickness.

2.2. Model compound of EP additives

Four types of sulfide (R-S_x-R) were chosen as test adsorbates. The purity and molecular structure of these compounds are shown in Table 1. They included organic oxide compounds and dissolved gases, and they were removed by repeated purification involving cyclic freezing with liquid nitrogen, evacuation and melting.

2.3. Experimental apparatus and technique

The experimental apparatus was shown in Fig. 1 and our previous report⁸⁻¹⁰⁾. The reaction chamber, with inner volume of about 1 liter, is made of stainless steel. Magnetic rotary drive is fixed to allow a metal specimen to drive from outside of the vacuum chamber, and an arm with a cutting tool made of ceramics (titanium nitride) is located.

Table 1 Structure and purity of organic sulfides

Rational formula	Purity
Ethyl sulfide $\text{CH}_3\text{-CH}_2\text{-S-CH}_2\text{-CH}_3$	>97%
Ethyl disulfide $\text{CH}_3\text{-CH}_2\text{-S-S-CH}_2\text{-CH}_3$	>99%
Allyl sulfide $\text{CH}_2\text{=CH-CH}_2\text{-S-CH}_2\text{-CH=CH}_2$	>98%
Allyl disulfide $\text{CH}_2\text{=CH-CH}_2\text{-S-S-CH}_2\text{-CH=CH}_2$	>75%

The chamber is evacuated by a rotary oil pump and an oil diffusion pump. After the pressure in the chamber became 1×10^{-4} Pa, the adsorbates was introduced into the chamber through a variable leak valve. When inlet gas flow is balanced by outlet flow, the pressure of the chamber became constant.

By rotating the specimen and thrusting the cutting tool, the nascent metal surface is exposed. The condition of frictional test was shown in Table 2. Although temperature at the sliding contact increases during sliding tests, molecules collide onto nascent surface apart from the contact. The adsorption process is not affected by frictional heating. The change of total pressure and partial pressure of adsorbates, caused by adsorption or reaction with nascent metal surface, could be monitored by a Bayard-Alpert ion gauge and a quadrupole mass spectrometer, respectively.

3. Result and discussion

3.1. Typical procedure for analysis

Figure 2 shows trace of intensity of fragment ions under diethyl mono-sulfide gas. We looked at the

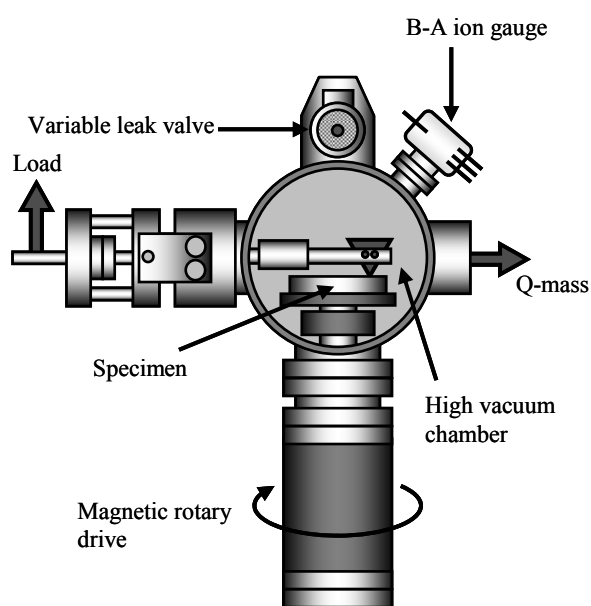


Fig. 1 Experimental apparatus

Table 2 Experimental conditions

Load, N	5.0
Cutting speed, cm/s	4.0-8.0
Partial pressure, $\times 10^{-4}$ Pa	2.7-6.0

molecular ion of diethyl mono-sulfide at mass-to-charge ratio (m/z) 90. The intensity of the molecular ion decreased exponentially as soon as the cutting test started. The results can be interpreted by adsorption of the sulfide gas on nascent metal surfaces that exposed by the test. Then the intensity of the molecular ion reaches a plateau. The result indicates a steady state where the rate of adsorption and the rate of nascent surface exposure reached equal. Since diethyl mono-sulfide adsorbed on the nascent metal surface, the intensity of molecular ion (m/z 90) started to decrease exponentially with cutting time. When it balanced between the adsorption of gas and production of nascent metal surface, the intensity kept a constant value. The intensity of the molecular ion turned to the initial value after the cutting was aborted. The ‘adsorption activity’ was calculated by the slope of semi-logarithmic relation of pressure decrease with cutting time. It is a parameter defining the strength of mutual interaction between a sulfide and a metal. The detail of calculation was explained in our previous reports⁸⁻¹⁰.

Careful analysis of mass spectrum revealed that several fragment ions were generated by decomposition of sulfides during the test. For example, ethane (R-H) at m/z 30, ethylene (R') at m/z 28 and butane (R-R) at m/z 58 were found as the reaction products of ethyl sulfides. Among them, generation of hydrogenated alkyl group was clear in comparison with the other hydrocarbons. Therefore, ‘Formation-Adsorption ratio’ was calculated based on the intensity of hydrogenated alkyl group (R-H: ethane from ethyl sulfides, propylene from allyl sulfides) ion and a sulfide molecule ion. The Formation-Adsorption ratio represents the rate of the C-S bond cleavage due to the rate determining step. It should be noted that the Formation-Adsorption ratio is closely related to the rate of iron sulfide generation²). Details of the mechanism and data processing procedure were reported previously⁸⁻¹⁰.

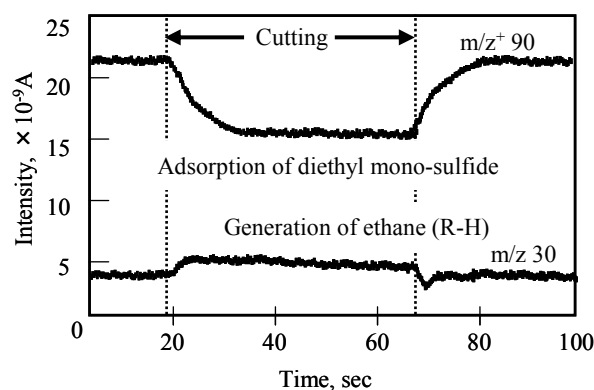


Fig. 2 Typical trace of fragment ions during current the copper surface

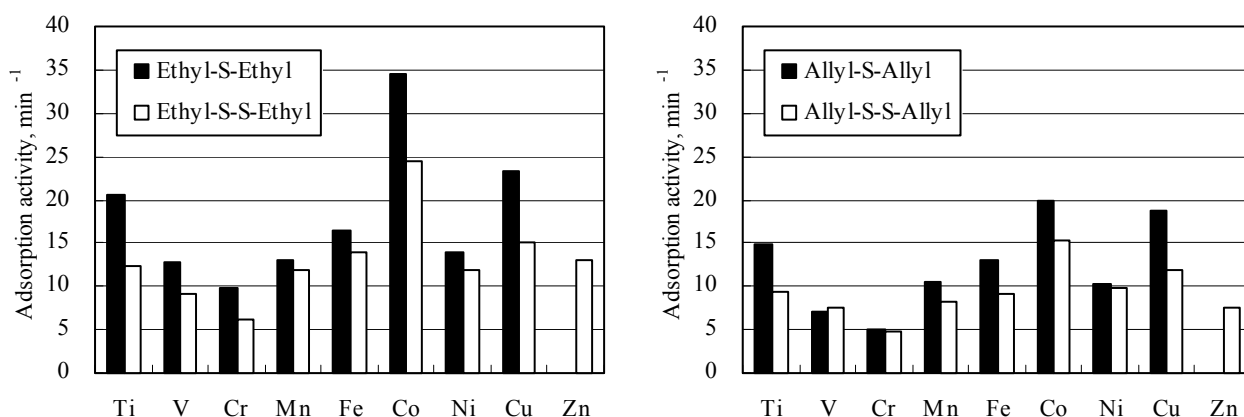


Fig. 3 Comparison of adsorption activity between metals

3.2. Adsorption activity

The adsorption activity of sulfides on nascent surfaces of transition metals was compared in Figure 3. The adsorption activity of sulfides on metals shows primarily the same tendency with an exception for Zn. Cobalt shows the highest adsorption activity while chromium shows the lowest. The adsorption of organic sulfides on nascent surfaces of transition metals is caused by the electron donation from sulfide to unoccupied d orbital as shown in Figure 4. Although chemical nature of unoccupied d orbital is related to the atomic number of the metals in the periodic table, it is noteworthy that Co exhibited the highest adsorption activity among the transition metals. The electronic structure of surface defects formed on the nascent surface may be related to the activity. Copper shows also high activity instead of a noble metal. We have

reported that benzene and olefins which have π -electrons chemisorbed on the nascent surface of gold as a noble metal¹¹⁾. This means that even gold becomes to be active chemically. Chemical nature of nascent metal surfaces is closely related to the electronic structure of surface defects formed by mechanical activation. A chemo-specific adsorption on Zn was observed; facile adsorption of disulfide was observed, while adsorption of mono-sulfides was undetectable. It is because that Zn is not a transition metal but a typical metals, the tendency of adsorption was different from other transition metals in orbital theory.

On the other hand, influences of alkyl group on adsorption activity were observed; the ethyl derivatives provided a higher adsorption activity than allyl derivatives regardless of mono- or disulfide. In our previous research¹¹⁾, it was found that the electron releasing from alkyl group to oxygen atom strongly afford the adsorption activity of alkyl ether. In this research, the presence of unsaturated bonds in the allyl group causes the weak electron releasing from alkyl group to sulfur atom rather than that of ethyl group. The model is illustrated in Figure 4a. On the other hand, comparing mono-sulfide and disulfide, it is found that mono-sulfide shows higher adsorption activity than that of disulfide regardless of the alkyl group. The results can be explained by the two electron-releasing groups for one sulfur atom in mono-sulfide, whereas there is only one electron-releasing per sulfur atom in disulfide. The model is illustrated in Figure 4b. It can be concluded that the chemisorption of organic sulfides on nascent metal surfaces is closely related to the density of lone pair electrons on sulfur atom.

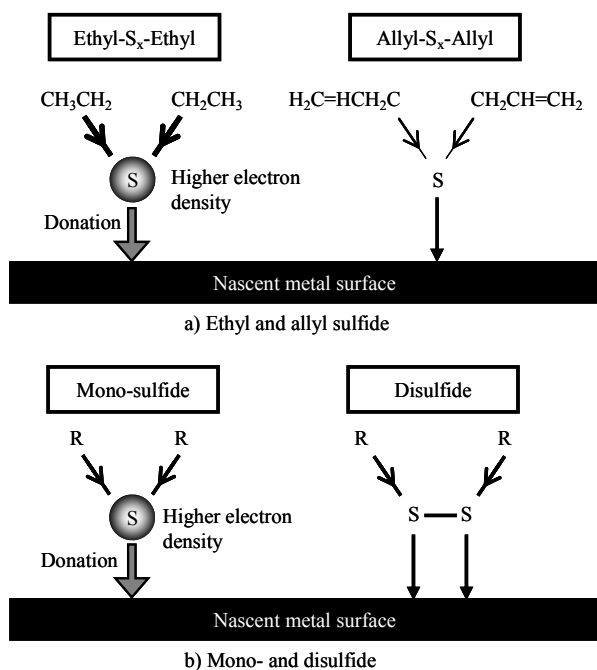
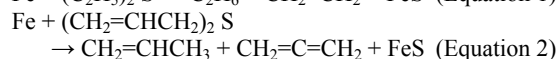


Fig. 4 Model illustration of adsorption on nascent surfaces

3.3. R-H Formation-Adsorption ratio

We found the generation of ethane (R-H) followed by the formation of metal sulfide by studying mass spectrum in Figure 2. A tribo-decomposition of sulfides was evaluated by the amount of alkane or alkene generation. The reactions are expressed by Equations 1 and 2.



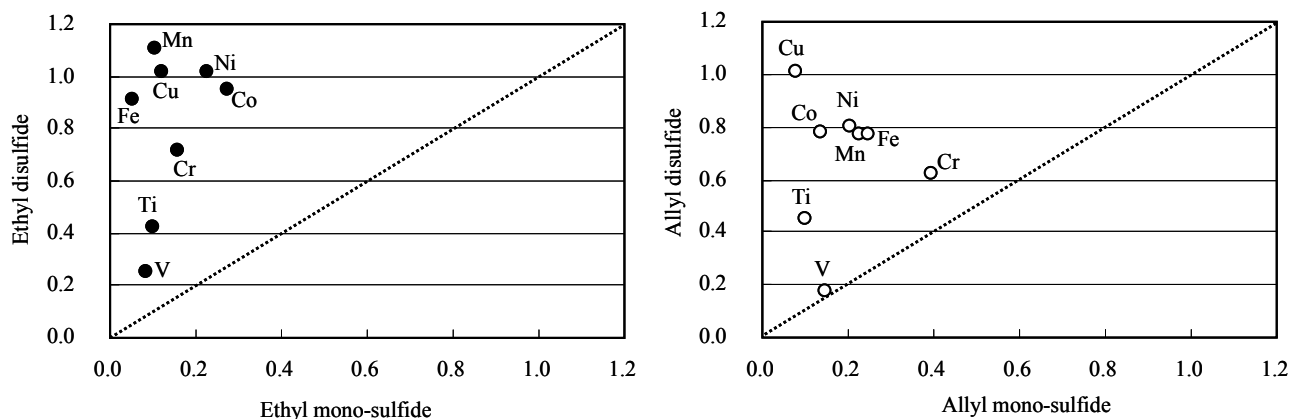


Fig. 5 Comparison of R-H Formation-Adsorption ratio

Figure 5 shows the formation of ethane or propene from diethyl or diallyl sulfides, respectively. The results indicate that diallyl sulfides decompose much faster than diethyl sulfides. The results can be explained by facile scission of carbon-sulfur bond at the allylic position. The model is illustrated in Figure 6. On the other hand, no obvious difference was observed between mono-sulfide and disulfide. According to the previous research²⁾, there should be scission of the S-S bond prior to the scission of the C-S bond. The scission of C-S bond is the rate-determining step in equation 1 and 2.

4. Conclusions

In this research, tribo-chemical reaction of organic sulfides was compared in terms of metal species. The tests were conducted to focus chemical reactivity of nascent surfaces. The observations of adsorption activity and Formation-Adsorption ratio of hydrocarbons are summarized as below.

1. Cobalt showed the highest adsorption activity for all the sulfides, whereas chromium showed the lowest adsorption activity. The same ranking between metals applied for almost all of the sulfides with the exception of zinc.
2. A unique characteristic for zinc was found; that is, almost no adsorption of mono-sulfides, and only the adsorption of disulfide was observed.
3. For both ethyl sulfides and allyl sulfides, the adsorption activity of the mono-sulfide was higher than that of disulfide.
4. For both mono-sulfides and disulfides, ethyl sulfide

showed higher adsorption activity than allyl sulfide.

5. Saturated hydrocarbons and olefins were formed during the adsorption process of the sulfides. Allyl sulfide showed higher tribochemical reactivity than ethyl sulfide.

5. Reference

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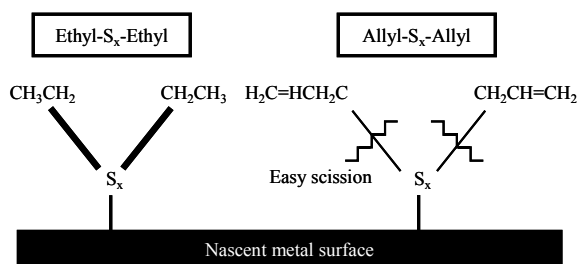


Fig. 6 Model illustration of C-S scission