Characterization of Tribofilm with the Remaining Lubricating Oil by Raman Spectroscopy

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As a first step to develop a method of in situ analysis of tribological behavior under oil lubrication, surfaces after the tribo-test with the remaining lubricating oil were analyzed with Raman spectroscopy. A ball-on-disk type tribo-test using a S45C disk and a SUJ2 ball was performed, and then its friction track of the disk surface was analyzed by Raman spectroscopy. Polysulfide and mineral oil were used as the lubricating oil without dilution. In addition to each lubricant peak, iron disulfide (FeS$_2$) tribofilm peaks were detected on the friction track in the case of polysulfide, whereas the magnetite (Fe$_3$O$_4$) peak was detected on the friction track in the case of mineral oil. FeS$_2$ intensity increased overtime in the case of the test at 200°C. In this way, tribofilm and oxide were detected as the remaining lubricating oil by Raman spectroscopy, which therefore suggests that Raman spectroscopy is an effective analysis method to investigate the formation process of tribofilm and oxide under oil lubrication.

Keywords: Raman spectroscopy, tribofilm, polysulfide, boundary lubrication, in situ

1. Introduction

To clarify the formation mechanism of tribofilms are important. Structures of tribofilms that formed on a friction surface in a lubricating oil are investigated by X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy, and time-of-flight secondary ion mass spectrometry [1-3]. Since these techniques require high vacuum environment, specimens are measured after the oil has been completely removed often by ultrasonic cleaning with an organic solvent such as hexane or acetone. However, it is possible that the tribofilms oxidize or degenerate during this washing process [4].

Fourier transform infrared spectroscopy (FT-IR) is a technique that uses light, and does not require high vacuum. It can be used in ambient air or under liquids. Therefore, this technique had been applied to in situ observations of the sliding interface. For example, Ichihashi et al. have recently investigated the concentration of additives in lubricant films at the contact interface [5]. FT-IR is used to obtain information about the functional group in organic compounds and is the best technique available for the detection of structural changes in lubricating oil. However, it is not capable of analyzing tribofilms that are mainly composed of inorganic compounds with weak infrared absorption.

Raman spectroscopy is a technique that is similar to FT-IR with respect to its use of light. This technique is used to obtain structures of inorganic compounds that are mainly detectable in the low frequency Raman region, and it has a high spatial resolution. Therefore, Raman spectroscopy has recently been used in the in situ measurement of friction surfaces [6-11]. For example, Singer et al. measured the dynamic change of the annealed boron carbide coating on Inconel substrates during a tribo-test [6], and Muratore et al. reported that molybdenum disulfide (MoS$_2$) changed to molybdenum trioxide (MoO$_3$) during a sliding test [9]. There are some reports about the structural changes of solid lubricants under dry conditions using in situ Raman tribometry. Furthermore, Joly-Pottuz et al. found the shear-induced structural modification of nanoparticles, tungsten disulfide (WS$_2$), and carbon nanotubes to be dispersed in polyalphaolefin (PAO) inside the contact area [10], and Bongaerts et al. investigated the thickness and concentration changes of glycerol inside the contact area [11]. The in situ Raman spectroscopy technique has been applied under oil lubrication. However, Joly-Pottuz et al. had investigated solid lubricants with oil, and Bongaerts et al. had applied the elastohydrodynamic lubrication regime. Both of them applied in situ techniques to the...
sliding interface including the lubricating oil, but these techniques had not been applied to the tribofilms created in boundary lubrication. In other words, there have been only few investigations of the tribofilms created from additives in the lubricating oil on the friction surface using in situ Raman spectroscopy techniques.

There are numerous reports with respect to tribofilms formed on steel by sulfur-containing extreme pressure additives. For example, Mori et al. mentioned that iron oxides, which include iron sulfide and iron sulfate, formed on steel in paraffin base oil containing 1 wt% polysulfide additive [1]. Toyoguchi et al. reported that sulfuric tribofilms were formed from organic peroxides by investigating the interactions of oxygen, sulfur compounds, and steel [12]. Therefore, the formation of sulfuric tribofilms on steel is closely related to oxidation reactions. However, the question remains whether the real surface states during friction were detected when ex situ analysis was performed after the tribo-test, because steel surfaces rapidly oxidize in the ambient air. It is important that in situ techniques be applied to friction interfaces in order to elucidate the formation mechanisms of tribofilms.

In this study, we investigated the possibility of detecting tribofilms formed from a sulfur-containing extreme pressure additive on carbon steel with the remaining lubricating oil using ex situ Raman spectroscopy. This is a preliminary study toward the development of in situ Raman tribometry. In addition, we investigated the possibility of analyzing oxide films using mineral oil.

2. Experimental method

Figure 1 shows a schematic of the ball-on-disk tribometer for all experiments in this study. Table 1 shows the chemical composition of the carbon steel (JIS S45C) disk material (Φ20 mm, 3 mm thickness). Bearing steel (JIS SUJ2) of 6.35 mm diameter was used as the ball. Disk surfaces were polished with 3 μm diamond abrasives and ultrasonically cleaned for 2 min prior to tribo-tests. The test oil used was polysulfide (di(tert-dodecyl)penta sulfide: C_{12}H_{25}-S_{5}-C_{12}H_{25}, 127 mm²/s kinematic viscosity (40°C)) as a sulfur-containing extreme pressure additive without dilution. Tests using mineral oil (30.6 mm²/s kinematic viscosity (40°C)) alone were performed as the comparison of the case of not forming tribofilms. Friction coefficient and width of friction tracks of the disks were measured at the condition that the load was 10 N with a friction speed of 1 cm/s at room temperature (25°C) and 200°C, with test times of 1, 5, and 20 min. Lubricating oils were continuously added at 7.5 ml/h to prevent drying on surfaces during the tests.

After the tribo-test, we measured the Raman spectra on the friction tracks and traced the formation of tribofilms and oxide films using micro-Raman spectrometer (LabRAM HR800, HORIBA, Ltd., Japan). Figure 2 shows the principle of Raman spectroscopy. When visible-light laser of frequency ν₀ irradiates a molecule, almost all photons are elastically scattered, as Rayleigh scattering, which is defined as the same frequency ν₀. Part of photons are inelastically scattered, as Raman scattering, which is defined by frequency ν₀ + ν relates to the molecular vibration. Raman spectroscopy can specify molecular structures from the ν.

Table 1 | Chemical composition of the disk material (mass%)
<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
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<tr>
<td>0.45</td>
<td>0.23</td>
<td>0.83</td>
<td>0.016</td>
<td>0.011</td>
<td>0.01</td>
<td>0.12</td>
<td>Bal.</td>
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they were analyzed in the presence of the remaining lubricating oils.

3. Results and discussion

3.1 Tribo-test

Figure 4 shows the friction coefficients during the ball-on-disk tribo-test. Friction coefficients in polysulfide and mineral oil at room temperature were under 0.2. The friction coefficient in mineral oil fluctuated more than that in polysulfide. Friction coefficients in polysulfide and mineral oil at 200°C were over 0.5. The friction coefficient in polysulfide rose to 0.7 within 1 min from the start and then remained stably between 0.5 and 0.6. On the other hand, the friction coefficient in mineral oil fluctuated between 0.6 and 0.7. It fluctuated more than that in polysulfide and showed spikes intermittently. Figure 5 shows width of the friction tracks. Compared with the room temperature data, the widths of the friction tracks at 200°C extended and the wear continued. This was attributed to the reduced viscosity of the test oils with increasing temperatures. Because a tribofilm formed in polysulfide, we expected that the friction coefficient decreased and tribofilm prevented the spread of the width of the friction track. However, the formation of tribofilms increased at 200°C, and which made it easy to flake. The repeated tribofilm growth and flaking caused corrosive wear. Consequently, the width of friction tracks was spread [13]. Figure 6 shows the disk and ball surfaces after the tribo-test (Fig. 4). The disk surfaces that used mineral oil turned black at 25 ºC and 200°C. The ball surface that used polysulfide at 200°C wore in a circular pattern and had scratches. In contrast, the ball surface that used mineral oil at 200°C wore in a half-moon-shape pattern that looks like adhesive wear. Adhesive wear did not occur in the polysulfide case from these observations of friction tracks of the balls. Consequently, the friction coefficients in polysulfide were stable.

3.2 Raman spectroscopy

It has been reported that iron oxide, iron sulfide, and iron sulfate were detected in tribofilms formed from polysulfide on carbon steel [1]. First of all, we measured the Raman spectra of standard powder specimens, α-Fe₂O₃, Fe₃O₄, FeSO₄·7H₂O, FeS, and FeS₂. Figure 7 shows the Raman spectra of FeS and FeS₂. FeS peaks were detected at 213 and 278 cm⁻¹, and strong FeS₂ peaks were detected at 337 and 371 cm⁻¹. These two iron sulfides can be distinguished from the positions and intensities of the peaks. For other specimens, α-Fe₂O₃ peaks were detected at 210 and 273 cm⁻¹, Fe₂O₃ peak was detected at 658 cm⁻¹, and FeSO₄·7H₂O peak was detected at 974 cm⁻¹. These results indicated that FeS and α-Fe₂O₃ cannot be distinguished, but FeS₂, Fe₂O₃, and FeSO₄·7H₂O can be distinguished from each other.

Figure 8 shows the Raman spectra on friction tracks of steel after the tribo-test at 200°C for 20 min. Surfaces were cleaned with acetone after tribo-test. Peaks at 339 and 373 cm⁻¹ were detected, as shown in Fig. 8(a). We considered that tribofilm comprised mainly FeS₂ from the results shown in Fig. 7 and the XPS analysis of the friction surface [14]. In addition, two broad peaks were detected between 1300 and 1600 cm⁻¹ (Fig. 8(a)). We considered that these peaks were the D and G bands [15]
attributed to the graphite structure from the peak positions and shapes. We also considered that polysulfide used to form the FeS$_2$ tribofilm was decomposed to hydrocarbons, and then the graphite was formed from the hydrocarbons. Therefore, we believe that these D and G bands were attributed to the decomposition of polysulfide. Although the FeS$_2$ peaks were detected where the tribofilm appeared flake (Fig. 8(b)), the intensities were less than 1/20 of intensities shown in Fig. 8 (a). This result implied that tribofilms tend to flake at high temperature, because the tribofilm had grown and become thicker. Raman spectrum on a polished surface is shown in Fig. 8(c). A very weak Fe$_3$O$_4$ peak was detected only at 660 cm$^{-1}$.

Figure 9 shows the Raman spectra on the friction track with the remaining oils. In the case of polysulfide at 200$^\circ$C for 1 min, the FeS$_2$ peaks were detected along with the polysulfide peaks. In the case of mineral oil at 25$^\circ$C for 20 min, the Fe$_3$O$_4$ peak was detected along with the mineral oil peaks. This result showed that Fe$_3$O$_4$ formed on the friction track in the mineral oil that has no oxygen atoms. The reason for this is believed that: oxygen in the ambient air was incorporated into the mineral oil by friction, and the dissolved oxygen in the mineral oil reacted with the steel surface. Therefore, Raman spectroscopy enables the detection of the FeS$_2$ tribofilm and Fe$_3$O$_4$ oxide film through the test oils.

However, in the case of polysulfide beyond 5 min and mineral oil anytime at 200$^\circ$C, the Fe$_3$O$_4$ peak was not detected because there was an increase in the background peaks. The Fe$_3$O$_4$ peak was covered with these background peaks. Figure 10 shows the Raman spectra on friction tracks after the tribo-test with mineral oil for 5 min at 200$^\circ$C. An Fe$_3$O$_4$ peak was not detected along with mineral oil, but it was detected after cleaning with acetone. The increased background peaks are attributed to the decomposition of test oils. This decomposed oils had the ability to fluoresce. Fluorescence background covered the wide range, to interfere with the Raman spectra.
scattering peaks.

Figure 11 shows the Raman spectra after 1, 5, and 20 min duration tribo-test. Figure 11(a)-(c) show the Raman spectra with the remaining oils. Figure 11(d) shows the Raman spectra after cleaning with acetone since mineral oil decomposed and affected the detection of Fe$_3$O$_4$ peak. FeS$_2$ and Fe$_3$O$_4$ peaks were detected in the polysulfide at 25°C (Fig. 11(a)). However, these peaks were much smaller than the polysulfide peaks. FeS$_2$ peaks were clearly detected in polysulfide at 200°C from 1 min to 20 min, as shown in Fig. 11(b). The Fe$_3$O$_4$ peak was detected in mineral oil after 5 min and becomes clear after 20 min at 25°C, as shown in Fig. 11(c). The Fe$_3$O$_4$ peak was detected after 1 min at 200°C (Fig. 11(d)).

Figure 12 shows the Raman spectra peak intensities of FeS$_2$ and Fe$_3$O$_4$ on the friction tracks, which were calculated from peak areas in Fig. 11. In the polysulfide case, FeS$_2$ intensities were weak at 25°C, and they were strong and increased rapidly with the sliding time at 200°C. Fe$_3$O$_4$ intensities at 200°C were constant and weaker than those at 25°C. In the mineral oil case, Fe$_3$O$_4$ intensities at 200°C were approximately constant and those at 25°C increased.

From these results, we conclude that the friction coefficient in the polysulfide case was more stable than in the mineral oil case, because thin films of FeS$_2$ and Fe$_3$O$_4$ formed and protected the steel surface at 25°C. The tribofilm had grown thicker by sulfuration at 200°C. Sulfuration occurred prior to oxidation, and the FeS$_2$ film repeatedly grew and flaked, generally called corrosive wear. Consequently, the friction coefficient increased because of the expansion of the friction track. However, we believe that corrosion wear prevents adhesive wear, and the fluctuation in the friction coefficient in polysulfide was smaller than that in mineral oil. In the case of mineral oil, although the surface had not been directly exposed to the ambient air, stable Fe$_3$O$_4$ was formed on the friction track. The oxide grew and the...
friction coefficient fluctuated widely at 25°C. Since the width of the friction track spread and the oxide intensities were almost constant at 200°C, the oxide grew and flaked repeatedly. The presence of the oxide caused adhesive wear, as concluded from the observation results of the ball surface in the mineral oil case at 200°C. We believe that the adhesion with oxide created a high friction coefficient.

4. Conclusions

We analyzed the tribofilms formed on carbon steel in the presence of polysulfide using Raman spectroscopy. The formation of tribofilms was detected with the remaining polysulfide. We found the possibility of in situ observation of tribofilms using Raman spectroscopy. We concluded the following:

(1) We detected FeS₂ tribofilm with polysulfide using Raman spectroscopy when the polysulfide did not decompose.
(2) We detected Fe₂O₄ oxide film with mineral oil that did not decompose. Because this oxidation resulted from friction despite there being no oxygen atoms in mineral oil, Fe₂O₄ was formed before cleaning with acetone.
(3) Oil decompositions were detected as background increase in both polysulfide and mineral oil at 200°C. Moreover, the D and G bands were simultaneously detected with tribofilm peaks after cleaning with acetone. We considered that these bands were attributed to the decomposition of polysulfide. We predict that the tribofilm and the decomposition of oils will be simultaneously detected by in situ measurement of friction surfaces using Raman spectroscopy.

References


