9-1 XANES Study of Tribofilms Generated from Continuously Variable Transmission Fluids

Recently, continuously variable transmissions (CVTs) have been attracting attention since they give better fuel efficiency than conventional automatic transmissions (ATs). Therefore, it has become very important for oil manufacturers to develop transmission fluids suitable for CVTs, that is, continuously variable transmission fluids (CVTFs) [1]. CVTFs are required to have a high friction coefficient with metal surfaces in order to transmit forces efficiently.

Physical properties of the fluids such as friction coefficients are expected to be governed by chemical species as well as by elements in tribofilms generated on the metal surface by lubrication. Therefore, in order to develop high-performance CVTFs, it is necessary to identify the chemical species present in the tribofilms. Conventional surface analysis techniques such as electron probe micro-analysis (EPMA) and X-ray photoelectron spectroscopy (XPS) have been employed to investigate the tribofilms, but their chemistry has not been well elucidated yet since the tribofilms are extremely thin and conventional analytical methods are not sensitive enough to allow chemical speciation.

XANES spectroscopy using synchrotron radiation is a powerful analytical technique, because it can detect very low-concentration elements in the extremely thin tribofilms, and is more sensitive to the chemical environments of elements such as S than any other analysis technique. Therefore, we have employed XANES spectroscopy to elucidate the chemistry of the tribofilms.

The tribofilms were prepared on steel blocks using a friction tester as shown in Fig. 1 [2]. Four different CVTFs, Fluids-1 to 4, were formulated with different additives such as friction modifiers and detergents as shown in Table 1. Fluids-1, 2 and 3 are designed for vehicles with high torque-capacity CVT units and have high friction coefficients. Fluid-4 is designed for vehicles with medium torque-capacity CVT, is also used as AT fluid, and has a medium friction coefficient. The S K-edge XANES measurements were carried out at BL-9A [3] using a Lytle detector in the fluorescence yield (FY) mode, to elucidate the chemistry of the bulks of the tribofilms.

As shown in Fig. 2(a), the FY-mode S K-edge XANES spectra of the tribofilms generated from Fluid-1 to 4 show different patterns, suggesting that the chemistry of the S species in the tribofilms are different. Each spectrum has four characteristic peaks (marked a, b, c and d). In order to identify the nature of these peaks, we also examined the S K-edge XANES spectra of the sulfur-containing model compounds predicted to

Table 1 Major additives and element concentration in CVTFs.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Fluid-1</th>
<th>Fluid-2</th>
<th>Fluid-3</th>
<th>Fluid-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction modifier</td>
<td>Zn type</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Friction modifier</td>
<td>organic type</td>
<td>x</td>
<td>o</td>
<td>x</td>
</tr>
<tr>
<td>Detergent</td>
<td>Ca type</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Detergent</td>
<td>Mg type</td>
<td>x</td>
<td>x</td>
<td>o</td>
</tr>
<tr>
<td>Element concentration (mass ppm)</td>
<td>S</td>
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<td>5000</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>290</td>
<td>620</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0</td>
<td>680</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
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<td>200</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
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<td>0</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>120</td>
<td>190</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>1100</td>
<td>900</td>
<td>900</td>
</tr>
</tbody>
</table>
Corrosion Protection of Steel by "Protective Rusts"

Loss due to steel corrosion is estimated to be equivalent to more than a few percent of Japan's GNP. Steel used with no coating has a high demand, not only due to its low costs, but also from materials life-cycle assessment consideration.

Weathering steel (WS) has been developed for the use in bridges without coating. WS, containing a 0.3-0.7 mass% of Cr and Cu, forms a protective rust layer after a few years of corrosion under atmosphere and the amount of corrosion is 1/5 that of normal mild steel (MS).

Macroscopic analysis has shown that the rust formed on WS is composed of fine grains to which can be attributed good corrosion resistance (Fig. 3). However, there has been little information on the mechanisms of how the addition of a small amount of other elements results in the formation of "protective rusts".

These mechanisms are investigated with special attention to reactions at the interface between liquids and a steel surface using various techniques at the Photon Factory [1,2]. The formation of colloidal rusts at an early stage of corrosion is investigated using ex and in situ [3] X-ray absorption fine structure (XAFS) measurements at BL-9A, 11B and 12C. The growth of protective rusts during wet-dry cycles is investigated using XAFS and generalized grazing-incidence-angle X-ray scattering [4] at BL-12C and 3A [1,5].

It has been shown that adding even a small amount of elements changes the initial process of corrosion drastically: the nucleation of the \( \text{Fe(O,OH)}_6 \)-network and its growth results in different morphology of the rusts grains (Fig. 4) [1,2,5].

The anodic corrosion reaction is simply expressed as follows:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe(OH)}_x \rightarrow \text{FeOOH}.
\]

When the reaction of rust formation is considered as the sum of nucleation and grain-growth, the total rate of reaction \( (\nu) \) can be written as follows:

References

\[ v = N \exp\left(-\frac{E_{\text{nuc}}}{kT}\right) \exp\left(-\frac{E_{\text{Growth}}}{kT}\right), \]

where \( N \) is the number of reaction sites, and \( E_{\text{nuc}} \) and \( E_{\text{Growth}} \) are the activation energies of nucleation and growth of the reaction products.

At the initial stage of corrosion, the Fe(O,OH)$_6$ units nucleate from Fe$^{2+}$. Alloy elements such as chromium increase the atomic level heterogeneity in rusts by occupying different sites in the network from that of iron; this leads to an increase in \( N \). It is also expected that the nucleation energy of the Cr(O,OH)$_6$ unit is lower than that of the Fe(O,OH)$_6$ and that this decreases \( E_{\text{nuc}} \). The increase of \( N \) and the decrease of \( E_{\text{nuc}} \) result in a situation where the speed of nucleation is larger than that of growth. This induces refinement of rust particles as small as a few nm (Fig. 4, top).

Contrary to this, the speed of corrosion (or growth) is large in MS. The reaction is nucleation-limited, and the rusts are composed of large grains containing many defects (Fig. 4, bottom).

A new concept of viewing corrosion as "evolution of the Fe(O,OH)$_6$-network" is proposed. In order to understand its mechanism, \textit{in situ} observation of the reaction at the interface between metal surfaces and liquid is essential, and such studies are expected to lead us to designing a new type of WS for the future.

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References