Synthetic Niobium Sulfide as a Solid Lubricant

Seiichiro HIRONAKA*, Masataka WAKIHARA* and Masao TANIGUCHI*

Niobium sulfide, Nb1.158S2, was synthesized by niobium pentoxide reacting with hydrogen sulfide at 700°C. Its lubricating properties were compared with those of molybdenum disulfide using a pendulum type friction tester and the Falex machine when they were added to the lithium soap/liquid paraffin grease. Niobium sulfide gave a lower friction coefficient and better extreme pressure properties than MoS2.

1. Introduction

Solid lubricants such as molybdenum disulfide and graphite have been added to lubricating oils and greases as additives, and used widely under conditions in which lubricating oils could not be used. The good lubricating properties of MoS2 and graphite are related to their layered crystal structures. In the study of the structures and bonding effects on the lubricating properties of crystalline solids1), Jamison has reported that molybdenum, tungsten, and niobium, which form dichalcogenides, have similar layered crystal structures and they are good solid lubricants. However, there have been very few studies on niobium sulfide as a solid lubricant2)-5). Lavik et al. have investigated the oxidation characteristics of NbS2 as a solid lubricant by means of thermogravimetric analysis (TG).2) The impurities which may influence the frictional properties of NbS2 have been investigated by TG.3) The friction characteristics of disulfides and diselenides of the second and third row transition metals from Group 4 through 7 have been studied on the solid films formed by burnishing them onto the frictional surface by hand with paper wipers.4) MoS2, WS2, NbSe2, MoSe2, WSe2 were good lubricants, but no lubricant film could be formed with NbS2. Therefore, NbS2 may rather be expected as an additive for lubricating oils and greases than as a solid lubricant film.

In the present study, niobium sulfide was synthesized by the reaction of niobium pentoxide with hydrogen sulfide, and its lubricating properties were investigated when it was added to the lithium soap grease.

2. Experimental

Niobium sulfide was prepared as follows. Commercially available high-purity grade (purity >99.9%) niobium pentoxide in a porcelain boat was kept in a hydrogen sulfide atmosphere at 700°C for 24 hr, as shown in Fig. 1. The product was quenched immediately and crushed in an agate mortar, and it was then reheated under the same conditions to ensure complete sulfurization.

The composition of niobium sulfide was determined by its weight change when it was oxidized to niobium pentoxide in air at 700°C for 48 hr6). The composition of niobium sulfide was Nb1.158S2. The particle size was 0.3–1 µm in diameter. Molybdenum disulfide (particle size, ca. 0.3 µm in diameter) which is a commercial solid lubricant was used as a reference.
Materials.

Liquid paraffin of the following properties: specific gravity, 0.884; pour point, -25°C; flash point, 220°C; viscosity, 76.0 cSt (at 37.8°C), was used as the base oil for the grease. Niobium sulfide and molybdenum disulfide (3 wt%) were added as solid additives to the lithium stearate/liquid paraffin grease (soap: 13 wt%) prepared in air.

Oxidation characteristics of niobium sulfide and molybdenum disulfide were examined by differential thermal analysis (heating rate in air: 5°C/min).

The friction properties of the base grease and those greases containing 3 wt% solid lubricant were examined in the temperature range from 23 to 110°C using a pendulum type friction tester. The extreme pressure tests were investigated with the Falex machine at 300 rpm. The tester was run at an initial load of 300 lbf for 2 min and then at 500 lbf for 1 min. After that the load was increased in increments of 250 lbf/min up to the seizure load.

3. Results and Discussion

Thermograms of niobium sulfide (Nb$_{1.158}$S$_2$) and molybdenum disulfide (commercially available MoS$_2$) by differential thermal analysis (DTA) are shown in Fig. 2. The oxidation temperatures of these solid lubricants from these thermograms are summarized in Table 1. The oxidation of Nb$_{1.158}$S$_2$ started at a lower temperature than that of MoS$_2$. This result was contrary to the results obtained for NbS$_2$ and MoS$_2$ by TG. This contradiction may be due to the structural difference between Nb$_{1.158}$S$_2$ and NbS$_2$. However, the lattice parameters and unit cell volumes of niobium sulfides hardly change with their composition. As shown in Fig. 2, two exothermic peaks, small (385°C) and large (525°C), were measured for MoS$_2$. The peak at the lower temperature may be due to the impurities, but it may depend on the oxidation temperature of commercial MoS$_2$. This fact should further be investigated in the future.

Figure 3 shows the friction characteristics of the base grease and greases containing 3 wt% solid lubricant in the temperature range from 23 to 110°C. Taking into consideration the oxidation stability of the base oil (liquid paraffin), both greases were heated up to 110°C. The friction coefficient of

![Figure 2 Thermograms of Nb$_{1.158}$S$_2$ and MoS$_2$ by DTA](image)

Test conditions: Heating rate, 5°C in air
Sample quantity, 0.08 mmol.

![Figure 3 Friction Characteristics of Nb$_{1.158}$S$_2$ and MoS$_2$](image)

Table 1 Oxidation Temperatures of Solid Lubricants

<table>
<thead>
<tr>
<th>Solid Lubricant</th>
<th>Oxidation Temperature (°C)</th>
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<tbody>
<tr>
<td>Nb$_{1.158}$S$_2$</td>
<td>345* 425</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>373* 385 525</td>
</tr>
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* Temperature at which an exothermic peak begins to appear due to oxidation.
the base grease decreased with increasing temperature. This is due to the decrease in the grease viscosity accompanied with the decrease in its viscosity resistance. It is considered that the grease viscosity decreased because aggregation between soap molecules was somewhat loose near 110°C above the first phase transition temperature, 104°C, of the grease. The friction coefficient did not change by cooling so much and it maintained low values because of the formation of lubricating films on the frictional surfaces by adsorption of the soap and/or oil molecules.

\( \text{Nb}_{1.158}\text{S}_2 \) and \( \text{MoS}_2 \) lowered the friction coefficient of the base grease considerably. It is well known that solid lubricants with layered crystal structures result in low friction because the layers slip easily by shear stress. At low temperature \( \text{Nb}_{1.158}\text{S}_2 \) gave a higher friction as compared with \( \text{MoS}_2 \), but showed a lower friction at higher temperatures above 80°C and by cooling. This may be due to the difference in the layered crystal structures as shown in Fig. 4. About 16\% of the niobium atoms in \( \text{Nb}_{1.158}\text{S}_2 \) occupy the partially-filled metal layers every second, but in \( \text{MoS}_2 \) the depleted layers are completely unoccupied. However, the explanation should be supported by future studies of \( \text{Nb}_{1.1+x}\text{S}_2 \) and \( \text{NbS}_2 \).

The extreme pressure properties of \( \text{Nb}_{1.158}\text{S}_2 \) and \( \text{MoS}_2 \) were compared by testing with the Falex machine. The remarkable effects of these solid lubricants were obtained on the load-carrying capacity of the greases (Table 2). With the base greases, seizure occurred at the first loading step of 300 lbf, while higher seizure loads were obtained with the solid-added greases. The higher seizure loads with \( \text{Nb}_{1.158}\text{S}_2 \) may suggest that niobium sulfides are equally as effective as \( \text{MoS}_2 \) as extreme pressure additives for greases.

Finally, when \( \text{Nb}_{1.158}\text{S}_2 \) was added to the grease, it gave a lower sliding friction and better extreme pressure properties than \( \text{MoS}_2 \). This seems to be due to the singular layered structure of \( \text{Nb}_{1.158}\text{S}_2 \). Thus, niobium sulfides could be expected as additives for lubricating greases. However, addition-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Lubricant & Seizure Load (lbf) \\
\hline
Base Grease & 300 \\
(liquid paraffin, 87 wt\%; lithium stearate, 13 wt\%) & \\
Base Grease + \( \text{Nb}_{1.158}\text{S}_2 \), 3 wt\% & 1,250 \\
Base Grease + \( \text{MoS}_2 \), 3 wt\% & 1,000 \\
\hline
\end{tabular}
\caption{Extreme Pressure Properties of Solid Lubricants}
\end{table}

\begin{center}
Fig. 4 Schematic Representation of the Sections through the (1120) planes of \( \text{Nb}_{1.1+x}\text{S}_2 \) and \( \text{MoS}_2 \)
\end{center}

\( \circlearrowleft \): Sulfur \( \circlearrowleft \): Niobium partially occupied. \( \bullet \): Niobium \( \bullet \): Molybdenum

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\section*{References}

要 旨

固体潤滑剤としての硫化ニオブ

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硫化ニオブ、Nb₁₁₅S₂ が 700℃における五酸化ニオブと酸化水素の反応によって合成された（Fig. 1）。Nb₁₁₅S₂ と市販の固体潤滑剤二硫化モリブデン、MoS₂ との融解特性が差異熱分析によって検討され、従来の結果と相反して Nb₁₁₅S₂ の方が融解安定性が低いことがわかった（Fig. 2, Table 1）。Nb₁₁₅S₂ および MoS₂ をそれぞれ 3 wt% ずつチウム石けん/流動パラフィングリースに添加したときの摩擦特性が振子型摩擦試験機によって、23〜110℃の温度範囲で比較された（Fig. 3）。無添加の場合、摩擦係数は温度の上昇とともに、グリースの粘度低下による粘性抵抗の減少によってかなり低下した。添加グリースでは、これらの添加剤の層状構造による潤滑性によって、摩擦は無添加のときよりかなり軽減された。MoS₂ より Nb₁₁₅S₂ の方が効果的であるのは、Fig. 4 に示すような構造との相違によるものと推察される。ファレックステストによる極圧性の比較でも、Nb₁₁₅S₂ が MoS₂ と同等以上の結果を示し、硫化ニオブは潤滑グリース用添加剤として十分期待される。

Keywords
Layered crystal structure, Molybdenum disulfide, Niobium sulfide, Solid lubricant