1. Introduction

In power machines such as engines, 10 to 15% of output is lost to friction at sliding members. Surface hardening techniques have been applied to obtain superior tribological characteristics (i.e., low coefficient of friction) of the sliding site. In recent years, nanostructures obtained by various deformation techniques have attracted much attention. In particular, surface grain refinement achieved by optimizing process conditions of a conventional deformation process is considered to be advantageous from a productivity perspective. For instance, a nanostructure obtained by using conventional techniques such as shot peening,\(^1,2\) burning,\(^3,4\) and deep rolling,\(^5,6\) and its improved tribological properties have been reported previously.\(^1-6\) We found that a nanostructured sample with high-density lattice defects (i.e., grain boundary and dislocation), which means the atomic configuration of the sample is disordered, showed a lower friction coefficient \(\mu\) during the ball-on-disk test under the lubrication of both poly-alpha-olefin (PAO) and ester oils.\(^5,7\) It can be hypothesized that a disordered atomic configuration at lattice defects will be expected to have a lower electron density compared with surrounding matrix, which may lead to a formation of electric dipole. The decrease of \(\mu\) is therefore possibly owing to a promoted formation of physiosorbed film of the oils on the surface of a sample originated from a van der Waals force.\(^5,7\)

However, as a component of a power transmission system, it is required to increase \(\mu\) value to improve the transmission efficiency. In order to achieve higher \(\mu\), an additive which forms a chemical reaction film on the surface is generally added to lubricant oil.\(^8-11\)

This study focuses on the promoted adsorption of lubri-
cating oil molecules by introducing high-density lattice defects, and tribological property of nanostructured steel under PAO oil with tricresyl phosphate (TCP), a typical additive which forms chemical reaction film, was investigated, together with the effect of lattice defects on the increment of μ.

2. Experimental Method

High carbon chromium JIS SUJ2 steel (SUJ2), which is widely used as a sliding member, was used as the test material. Ultra-low carbon steel (ULC), which can eliminate the influences of impurities and precipitates, was also used as a test material. Compositions of each material are shown in Table 1. Initial microstructure of the SUJ2 was tempered martensite with spherical carbides having a diameter of about 1 μm, and Vickers hardness Hv of the SUJ2 was 7.4 GPa. The ULC was annealed at 1 000°C for 3.6 ks in a vacuum prior to the experiments (Hv 0.6 GPa).

The SUJ2 was subjected to the surface-nanostructured wearing (SNW) process to obtain nanostructure on the surface. In the SNW process, a lateral face of cemented carbide (WC-Co) tipping tool was pressed to a rotating disk, which led to the introduction of large shear deformation in the surface of the sample, followed by significant grain refinement. The SNW process was performed with a pressing load, feeding speed, rotation speed, and pressing time of 500 N, 0.01 mm/rev, 1 600 rpm, and 20 s respectively, and a water-soluble emulsion was used as a coolant during the process.

In case of the ULC, nanostructure was obtained by using a high-pressure torsion (HPT) process, which is a severe plastic deformation (SPD) technique. In the HPT process, a disk-shaped sample was placed between two anvils with a depression of 0.25 mm in depth, and subjected to torsional shear strain by rotating the lower anvil under a high compressive pressure on the order of GPa. The sample size was observed at 1 000°C for 3.6 ks in a vacuum prior to the experiments (Hv 0.6 GPa).

The SNW process was performed with a pressing load, feeding speed, rotation speed, and pressing time of 500 N, 0.01 mm/rev, 1 600 rpm, and 20 s respectively, and a water-soluble emulsion was used as a coolant during the process.

Table 1. Compositions of steels.

| JIS SUJ2 bearing steel [mass%] | C | Si | Mn | P | S | Ni | Cr | Mo |
|-------------------------------|---|----|----|---|---|----|----|----|
| 1.00                          | 0.20 | 0.41 | 0.014 | 0.009 | 0.08 | 1.37 | 0.03 |

| Ultra-low carbon (ULC) steel [mass ppm] | C | Si | Mn | P | Al | Ti | Cr | B | N | O |
|----------------------------------------|---|----|----|---|----|----|----|---|---|---|
| 11 < 30 < 20 < 3 300 < 20 < 30 < 2 | 8 | 14 |

3. Results and Discussion

3.1. The Increased Coefficient of Friction μ in the Surface-nanostructured High Carbon Chromium JIS SUJ2 Steel

Figure 1 shows a cross-sectional SEM image of the SUJ2 sample after the SNW process observed near the surface of the sample. The uniform nanostructured layer can be observed from the surface to a depth of about 4 μm. In this study two different HPT processes, monotonic-HPT (mHPT) and cyclic-HPT (cHPT), were performed to control the grain size of the sample by switching the shear direction (i.e., rotation direction of the lower anvil) during the process. The mHPT process introduced shear strain into the sample by rotating the lower anvil N rotations without switching the shear direction throughout the process. In the cHPT process, the shear direction was switched to the opposite direction after rotating certain N (N = 1/8 was employed in this study), and this procedure was repeated until total N reached to an objective N (N = 10). After the HPT process, low temperature annealing at 200°C for 1 h was performed to control the dislocation density in the sample while keeping the grain size. The annealed sample was referred to as HPT+A.

Friction coefficient μ was measured by ball-on-disk test. The test was performed at room temperature, and SUJ2 or Al2O3 used as a ball material. The load, sliding speed, and sliding radius for the ball-on-disk test were 200 g, 10 mm/s, and 5 mm respectively. Poly-alpha-olefin (PAO) and tricresyl phosphate (TCP, C8H2O3P) added PAO oils were used as lubricants during the ball-on-disk test. Table 2 shows the properties of PAO oil. The ball-on-disk test was started immediately after the sample was soaked in the lubricant oil expect for the results shown in Fig. 3. Some wear was observed after the ball-on-disk test in any of the samples after the test.

Table 2. Characteristics of lubricant.

| Lubricant | Kinematic viscosity @ 40°C [mm²/s] | Kinematic viscosity @ 100°C [mm²/s] | Viscosity index | Density @ 15°C [g/cm³] | Refractive index @ 20°C | Major ingredient | Chemical formula | Structural formula |
|-----------|----------------------------------|-----------------------------------|----------------|------------------------|------------------------|-----------------|-----------------|------------------|
| PAO (Poly-α-Olefin 17) | 17.38 | 3.925 | 122 | 0.8187 | 1.4552 | 1-Decene (Trimer) | C8H16 | |
In the non-deformed sample showed a constant value at around 0.13 from the beginning of the test. The \( \mu \) gradually increased from a sliding distance of 1 000 m and reached a value of around 0.15. However, in the SNW-processed sample, whereas the initial \( \mu \) value was almost the same as that of the non-deformed sample, the \( \mu \) of the SNW-processed sample showed a notable increase with increasing sliding distance and reached a value of about 0.2 at the sliding distance of 500 m or higher. Figure 3 shows the ball-on-disk test results of the sample under the TCP added PAO lubrication with a soaking time of 14 h before the test. By soaking the samples to the lubricants, the \( \mu \) value of the samples increased the sliding distance from the beginning of the test even in the non-deformed sample, and the \( \mu \) value reached a final value of 0.25, which was higher value than the value obtained in the test without a soaking time.

The results showed that \( \mu \) during the ball-on-disk test under the PAO and ester lubrication was decreased by increasing the density of lattice defects (disordered atomic configuration). This was thought to be due to the promotion of the physisorbed film formation.\(^5\)\(^7\) On the basis of the above results, we considered a mechanism to increase \( \mu \). The mechanical shear applied during the ball-on-disk test caused a decomposition of TCP molecules in the PAO oil, and an adsorption of the decomposition product to the sample surface was promoted by the nanostructure, resulting in the formation of a chemical reaction film. When the sample was subjected to sufficient soaking time prior to the ball-on-disk test, TCP molecules could be adsorbed on the sample surface before the test. The adsorbed TCP molecules were decomposed on the sample surface and instantly formed a chemical reaction film. The samples therefore showed the same \( \mu \) values irrespective of the presence of the nanostructure. The increase of \( \mu \) with sliding distance suggested that the mechanical shear was required to decompose TCP molecules to form a chemical reaction film. From the adsorption perspective, it was necessary to consider the effect of the roughness of the surface.\(^{11}\) The surface roughness of SUJ2 after the SNW process was estimated by arithmetic mean roughness \( R_a \) and was 1.4 \( \mu \)m, which was larger than that of the non-deformed sample (\( R_a = 0.5 \mu \)m). Since the surface area increased with \( R_a \), it can be expected that the frequency of adsorption would be high in the SNW-processed sample, and the formation of the chemical reaction film be promoted in the SNW-processed sample. By employing the soaking time, however, both samples showed almost the same \( \mu \) value. The influence of surface roughness on the increase of \( \mu \) therefore seemed to be small.

### 3.2. Effect of High-density Lattice Defects on High Coefficient of Friction in Nanostructured Ultra-low Carbon Steel

From the ball-on-disk test of SUJ2 samples under TCP-added PAO lubrication, it was found that the nanostructure caused an increase of \( \mu \). We investigated the effect of lattice defects on tribological property by changing the density of lattice defects in the ULC samples, using the HPT-process

![Fig. 1. SEM image near the surface of SUJ2 steel after SNW (Surface-Nanostructured Wearing) process.\(^5\)](image)

![Fig. 2. Changes of the coefficient of friction during ball-on-disk test under TCP (TriCresyl Phosphate) added PAO (Poly-\( \alpha \)-Olefin) lubrication in the SUJ2 steel disks before/after SNW process. Ball: SUJ2 steel. (Online version in color.)](image)

![Fig. 3. Changes of the coefficient of friction during ball-on-disk test under TCP added PAO lubrication after soaking for 14 h in the SUJ2 steel disks before/after SNW process. Ball: SUJ2 steel. (Online version in color.)](image)
and subsequent annealing. The Al₂O₃ ball was employed as the ball for the ball-on-disk test. As mentioned above, TCP molecule decomposes and forms a chemical reaction film on the sample surface, which greatly affects the tribological property.⁸,¹⁰ To emphasize the effect of high-density lattice defects, Al₂O₃ was chosen as the ball material because a chemical reaction film was not formed on the Al₂O₃ surface.

Vickers hardness of the samples after the cHPT- and mHPT-processes was unchanged with \( N \) of more than 10 cycles, meaning that the structural change during the HPT process was saturated. Figure 4 shows the inverse pole figure (IPF) maps of the ULC samples before and after the HPT-process and annealing process. The microstructures were observed from a direction parallel to the rotation axis of the HPT process at \( r = 5 \) mm region where the ball-on-disk test was performed. From the IPF maps, the grain size \( d \) was estimated by the equivalent circle diameter. The volume fraction of grain boundary \( V_{gb} \) was calculated by the following method. It is known that grain boundary area per unit volume \( S \) in a microstructure having arbitrarily-shaped crystal grains can be expressed by \( S = 2/L \), where \( L \) shows three-dimensional average intercept length. The relationship between \( d \) and \( L \) is also given as \( d = CL \). Here, \( C \) is a constant related to shape anisotropy of crystal grains. Since the sample had equiaxed grain, the shape anisotropy in the microstructure of the sample was small, and \( C \) was therefore regarded as 1. From these relations, \( V_{gb} \) was calculated by assuming that the grain boundary thickness was 1 nm. Dislocation density \( \rho \) of the HPT-processed samples before and after the annealing process was calculated by XRD profile

![Figure 4](image_url)

**Figure 4.** SEM/EBSD IPF (Inverse Pole Figure) maps of ULC steels after HPT-straining and annealing: (a) non-deformed, (b) cHPT, (c) mHPT, (d) cHPT+A and (e) mHPT+A specimens. (Online version in color.)

**Table 3.** Microstructural characteristics of ULC steels after HPT-straining and annealing.

| Sample     | Vickers hardness \((r = 5 \text{ mm})\) | Grain size \((r = 5 \text{ mm})\) | Volume fraction of grain boundary \(V_{gb}\) | Dislocation density \((r = 5 \text{ mm})\) \(\rho\) \(\text{[m}^{-2}\]\) |
|------------|------------------------------------------|-----------------------------------|---------------------------------|---------------------------------|
| Non-deformed | 0.6 | 430 000 | 0.00047 | 5.0 \times 10^{13} |
| cHPT       | 3.1 | 550 000 | 0.36 | 4.5 \times 10^{14} |
| mHPT       | 3.5 | 320 000 | 0.63 | 4.3 \times 10^{14} |
| cHPT+A     | 2.9 | 590 000 | 0.34 | 5.0 \times 10^{13} |
| mHPT+A     | 3.4 | 360 000 | 0.56 | 7.9 \times 10^{14} |
analysis using Williamson and Smallman method.\textsuperscript{20} The sample for the XRD measurement was an 8 mm diameter disk centered at \( r \) of 5 mm, and the surface was finished by electropolishing. Table 3 shows the microstructural characteristics of each ULC sample. The \( d \) is reduced to about 1/1 000 compared with \( d \) of non-deformed sample after the HPT process, and the \( V_{gb} \) also increased. In addition, no remarkable grain growth or softening by the annealing was confirmed in either the chPT or mHPT samples, whereas \( \rho \) decreased to about 1/10.

Using these samples, the effect of lattice defects on tribological property was investigated by the ball-on-disk test under the PAO and TCP-added PAO lubrication. The ball-on-disk sample was polished using \#800\quad\text{waterproof abrasive paper in order to unify the surface roughness of the samples. The obtained} \( R_a \) \text{values showed no apparent difference between the samples, and the values measured perpendicularly and parallel to the polishing traces were approximately 0.07 and 0.05 \( \mu \text{m} \), respectively.}\textsuperscript{5}

Figure 5 shows the ball-on-disk test results under PAO lubrication in the non-deformed and mHPT-processed samples. These samples had largest difference in lattice defects density among the samples prepared in this study. There was no significant change in \( \mu \) value under PAO lubrication. However, under the lubrication of TCP-added PAO, the \( \mu \) value showed an increase with decreasing \( d \) or \( V_{gb} \) (Fig. 6) and with increasing \( \rho \) (Fig. 7) from the beginning of the test. The difference in texture between the mHPT and chPT samples possibly affect the tribological property, but no clear texture difference was observed in the XRD profiles. It can be therefore concluded that increase of \( \mu \) is caused by the introduction of high-density lattice defects.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph1.png}
\caption{Changes of the coefficient of friction during ball-on-disk test under PAO lubrication in the ULC steel disks before/after HPT (High-Pressure Torsion)-straining. Ball: Al\(_2\)O\(_3\). (Online version in color.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph2.png}
\caption{Changes of the coefficient of friction during ball-on-disk test under TCP added PAO lubrication in the ULC steel disks before/after HPT-straining. Ball: Al\(_2\)O\(_3\). (Online version in color.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph3.png}
\caption{Changes of the coefficient of friction during ball-on-disk test under TCP added PAO lubrication in the ULC steel disks before/after HPT-straining and subsequent annealing. Ball: Al\(_2\)O\(_3\). (Online version in color.)}
\end{figure}
Figure 8 shows back scattering electron (BSE) and secondary electron (SE) images at the sliding surface in the ULC steel samples after the ball-on-disk test (Sliding distance: 1 000 m) under TCP added PAO lubrication. From the BSE image, where contrast is sensitive to composition, a dark gray region was observed in the wear tracks formed along sliding direction of the ball (Figs. 8(a), 8(b)). The dark gray region is larger in the non-deformed sample than in the mHPT-processed sample. Moreover, when the dark gray region was observed by SE, which is sensitive to irregularities, many cracks were observed (Figs. 8(c), 8(d)). These results suggest that the dark gray region consisted of hard and brittle material, and the sample exhibited a high $\mu$ by abrasive wear. Figures 9 to 11 show the results of STEM observation and EDX analysis in a sample picked up from the black region using the FIB micro sampling method. The sliding direction of the ball is perpendicular to the paper surface. The sample surface was protected by a carbon deposition film with a thickness of several $\mu$m. The chemical reaction film with a thickness of about 200 nm was observed on the surface of the steel (see Fig. 9). The streaky defects observed at the interface between the chemical reaction and carbon deposition films are formed during the FIB process and allows us to detect the surface of the chemical reaction film formed by the ball-on-disk test. As shown in the SAD pattern in Fig. 9, the ring-like pattern with clear diffraction spots showed that the chemical reaction film was composed of grains with a size of several nm. The element maps of Fe, O, and P shown in Figs. 10 and 11 revealed that the chemical reaction film had lower Fe and higher O contents comparing with the matrix. Although no apparent difference could be seen in the P content in
the elemental map, it could be seen that the P content was markedly higher in the chemical reaction film by normalizing the EDX spectra by Fe intensity obtained from the red and blue rectangle regions. Ga detected in the EDX spectra was introduced during the FIB process, and Mo in those is a mesh material which is used to fix a STEM sample. It was thought that the thickness at the chemical reaction film region became thinner comparing with that at matrix during sample preparation using FIB, and the difference could not be seen in the element map in spite of higher P content.
at the chemical reaction film. These results were common for both non-deformed (Fig. 10) and mHPT-processed (Fig. 11) samples. However, the observed P content was lower than the expected value assuming that the constituent phase of the chemical reaction film was iron phosphate, such as FePO₄ and Fe₃(PO₄)₄. Although the SAD pattern shown in Fig. 9 has been being analyzed, the constituent phase cannot be identified at this moment.

From the above results, the high μ value was presumed to have been obtained from the abrasive wear of the nano-grained chemical reaction film, which consisted of an Fe–O–P-based compound formed during the ball-on-disk test. In case of the non-deformed sample, the formed Fe–O–P-based compound was easy to embed in the matrix during the ball-on-disk test because of its low hardness. Since the mHPT sample has high hardness, however, the Fe–O–P-based compound was difficult to embed in the matrix, resulting in a significant abrasive wear of the compound. Consequently, many dark gray regions were widely dispersed in the non-deformed sample from the BSE image on the sliding surface compared to the mHPT sample (Figs. 8 and 9). With an increasing sliding distance, μ of the non-deformed sample gradually increased and showed an almost identical μ value of 0.3 to that of the mHPT sample. The STEM image in Fig. 9 indicates that the surface of the non-deformed sample after the ball-on-disk test had a similar grain size to the mHPT sample, which suffered severe plastic deformation during the ball-on-disk test. Hence the Fe–O–P compound became difficult to be embedded to the matrix phase with the increase in the hardness of matrix, and μ of the non-deformed sample gradually increased with sliding distance and showed the same value with the mHPT sample at the sliding distance of 1 000 m.

4. Summary

In this study, the effect of lattice defects on an increase of coefficient of friction μ in steel under the TCP added PAO lubrication was investigated. The results are shown below.

- The μ of the high carbon chromium JIS SUJ2 steel, which surface layer was refined to a grain size of tens of nm by the SNW-process, was higher than that of the non-deformed sample, which had no nanostructure.
- By introducing high-density lattice defects (volume fraction of grain boundary V_gb and dislocation density ρ), the ULC steel, where the influence of impurity elements was reduced, showed a higher coefficient of friction and reached maximum μ value at an early stage of the test.
- During the ball-on-disk test, an Fe–O–P compound consisting of nano-grains was formed on the surface, and it seemed that the high μ values were achieved by abrasive wear of the compound.

- Further exploration of the formation and tribological behaviors of the Fe–O–P compound and their relation to the change of μ, is needed, and we hope to investigate this in the near future.

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