A Study of Hot Rolling Oil with Calcium Carbonate for Stainless Steel Process

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Dispersion-type lubricants formulated with calcium carbonate were experimentally studied to achieve improved hot-rolling characteristics of stainless steel. Two types of lubricants; over-based calcium sulfonate dispersed in oil (fluid type; FT) and calcium carbonate dispersed in grease (semi fluid type; ST) were prepared. ST containing larger particles of calcium carbonate exhibited a better lubricity in rolling of steel than FT. Although the particle size of calcium carbonate powder is about 1 μm , the dispersed state was stable in ST. Following the rolling tests, the surfaces of tribo-films were analyzed using XPS and TOF-SIMS. A lubrication model with calcium carbonate particles was proposed based on the surface analysis.

Keywords: hot rolling, stainless steel, seizure, calcium carbonate, grease, over-based calcium sulfonate

1. Introduction

Rolling is a metal working process where large pieces of material are deformed between rolls to form desired thinner cross sections. In hot rolling of steel, workpiece materials are heated to about 1000 °C and rolled under a load of tens of meganewtons. The rolled material surface exposed to the extreme rolling conditions can undergo seizure. It is well known that seizure often occurs in hot rolling of stainless steel possibly because, compared to carbon steel, an oxide film on a stainless steel surface is thinner and nascent surfaces are more likely to be generated during rolling¹⁾. Once the work roll seizes with the rolled strip, the seized strip starts to be stacked in layers on the roll surface. As rolling proceeds, repeated friction allows the pieces of the seized strip to break off the roll surface, leading to roll surface damage^{2,3)}. Seizure on stainless steel surfaces is not only a cause of such damage, but in shorter intervals of roll replacement or polishing, a slowdown in production and a shorter life of the rolls.

Many attempts have so far been made in the steel industry to prevent seizure of stainless steel by selecting a workpiece or roll material, a rolling speed, a heating temperature and a rolling reduction⁴⁻¹⁰⁾. In addition, several studies about solid lubricants to prevent seizure including iron oxide, black lead, mica, potassium phosphate and engineering plastic powders were reported¹¹⁻¹⁷⁾. On the other hand, Izawa et al. have

evaluated an oxalic film to be formed on a roll surface¹⁸⁾.

The aim of this study is to prevent seizure in hot rolling of stainless steel with new lubricants. The lubricants were formulated with calcium carbonate as it is inexpensive, easily-available and environmentally-friendly without producing harmful gas by heating.

2. Experiments

2.1. Specimens

Two lubricants were tested. A semi-fluid type lubricant (ST) was prepared by dispersing calcium carbonate powders having a diameter of 1 μm in a grease thickened by lithium 12-hydroxyarate (LiOHSt). A fluid type lubricant (FT) was the oil dispersed with over-based calcium sulfonate (OBCS) having a diameter of about 15 nm. Tables 1 and 2 show the composition and the property of the two lubricants. ST contains 0-60 mass% of calcium carbonate powder and 1.3 mass% of LiOHSt. FT contains 0-30 mass% of calcium carbonate and 5-16 mass% of calcium sulfonate. A combination of mineral oils with varying viscosity was added to both lubricants to achieve desired unworked penetration and kinematic viscosity, which were equivalent to NLGI grade of No.000-No.0 and 250-260 mm²/s, respectively, to facilitate smooth pumping by a regular pump.

2.2. Hot rolling test

The tests were carried out under the conditions described in Table 3. The strips of stainless steel (JIS SUS444: $5.4 \times 25 \times 100$ mm) and carbon steel (JIS SS400: $4.0 \times 25 \times 100$ mm) were heated to 1000 °C and 900 °C, respectively, in a nitrogen atmosphere in an infrared furnace and rolled using a 2Hi rolling mill. The JIS SKD11 roll was used. The size of the roll is 150 mm in diameter and 150 mm in width. The surface roughness of the roll is about 1 μm (R_a), and is comparable to that of a roll used in actual rolling. In fact, our experiments were started with High Speed Steel (HSS) rolls which are the most widely used roll material in hot rolling. However, the experiments had to be discontinued since HSS rolls had cracks accompanied by seizure when stainless steel strips were rolled. Instead, the subsequent experiments were performed with JIS SKD11 rolls which are typically used in cold rolling so there was almost no crack following seizure.

The lubricants were applied directly onto the roll to form a lubricant film of 5 μm . Rolling force during the test was measured by a load cell. After testing, the thickness of the rolled strips was measured using a micro gauge. The rolled strip surfaces were analyzed by EPMA, XPS and TOF-SIMS.

3. Results and discussion

3.1. Effects of calcium carbonate on carbon steel rolling

Although the objective of this study was to prevent seizure in hot rolling of stainless steel, the experiments were started with carbon steel strips. Carbon steel strips are highly resistant to seizure and can provide a definitive comparison between the two lubricants, a dispersed grease with calcium carbonate (ST) and a dispersed oil with over-based calcium sulfonate (FT), under seizure-free conditions. Their lubricity was evaluated based on the measurements of rolling force.

Figure 1 shows rolling force measured in carbon steel rolling. The white circles and the black squares represent rolling force with ST and FT respectively. ST decreased rolling force with an increase in calcium carbonate content. The rolling force stayed fairly constant when it contained more than 30 mass% of calcium carbonate. As for FT, the rolling force varied to a considerable extent and was greater than that measured with ST having the same amount of calcium carbonate. These results revealed that in hot rolling of carbon steel ST is more effective in achieving stable rolling than FT with the same amount of calcium carbonate.

Table 1 Composition and consistency of ST samples

	ST0	ST10	ST20	ST30	ST40	ST50	ST60
CaCO ₃ , mass%	-	10	20	30	40	50	60
LiOHSt, mass%	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Mineral Oil, mass%	98.7	88.7	78.7	68.7	58.7	48.7	38.7
Unworked Penetration, -	452	449	446	418	394	383	365

Table 2 Composition and kinematic viscosity of FT samples

	FT0	FT10	FT20	FT30
CaCO ₃ , mass%	-	10	20	30
Ca Sulfonate, mass%	-	5	11	16
Mineral Oil, mass%	100	85	69	54
Kinematic viscosity @40 °C, mm ² /s	251	254	253	257

Table 3 Test condition

Roll		
Material	JIS SKD11	
Dimension	150 ϕ $\times$ 150 mm	
Roughness (R_a)	1.04 μm (Top) 1.01 μm (Bottom)	
Speed	0.24 m/s(30 rpm)	
Gap	3.5 mm	
Strip		
Material	JIS SS400	JIS SUS444
Dimension	$4.0 \times 25 \times 100$ mm	$5.4 \times 25 \times 100$ mm
Temperature	900 °C	1000 °C

Fig. 1 Rolling force in carbon steel

3.2. Lubricity of base lubricant in stainless steel rolling

Following the above tests, as a first trial, ST and FT with 30 mass% of calcium carbonate were evaluated in hot rolling of stainless steel because conventional OBCS generally contains only up to 30 mass% of calcium carbonate.

As in rolling of carbon steel, lower rolling force was measured with ST (ST30: 52 kN, FT30: 66 kN). Meanwhile, seizure occurred in the stainless steel strips lubricated with FT and ST, but was severer in the strips with FT. In hot rolling of stainless steel, ST exhibited better lubricity to reduce rolling force and seizure than FT.

According to the surface inspection with a microscope, ST with 30 mass% of calcium carbonate prevented seizure more effectively than FT, but was not capable of completely eliminating seizure. Consequently, STs with calcium carbonate content higher than 30 mass% were evaluated as a possible solution to improve seizure resistance. It should also be mentioned that no further evaluation was performed with FT.

3.3. Seizure resistance by calcium carbonate powder

Hot rolling tests using stainless steel strips lubricated with STs were conducted to study the effects of calcium carbonate content. The calcium carbonate content in STs was changed ranging from 0 to 60 mass% by 10 mass% increments.

Figure 2 shows the roll surface after rolling tests. The roll surface lubricated with ST0 having 0 mass% of calcium carbonate had seizure on most of the surface. However, STs exhibited higher seizure resistance with an increase in calcium carbonate content, and almost no seizure was observed when the content was more than 50 mass% (ST50, ST60).

Figures 3 and 4 show a correlation between the thickness of rolled strips and calcium carbonate content, and changes in rolling force through rolling time, respectively. Although the roll gap was fixed through the tests, the rolled strip thickness and rolling force decreased with an increase in calcium carbonate content. That means that the high content of calcium carbonate contributes to improve hot rolling characteristics of stainless steel. In addition, Figure 4 indicates that rolling time was reduced as calcium carbonate content decreased even when strips of the same length were rolled. Such a reduction in rolling time, which was associated with increased rolling force, could be explained as follows; the seizure-damaged strip with lower calcium carbonate content was caught up between rolls and can hardly be extended in the rolling direction.

Figure 5 shows the effects of calcium carbonate content on rolling effectiveness. It was found that the rolling force and the reduction were affected by the content of calcium carbonate in ST. Therefore, the effectiveness of ST was evaluated by the ratio of the rolling force and the reduction as shown in Figure 5. STs exhibiting the lower rolling effectiveness were

considered to have better lubricity. As for STs with more than 50 mass% of calcium carbonate, which showed almost no seizure as shown in Figure 2, the rolling force decreased by about 40% compared to ST without calcium carbonate. It is obvious that the lower rolling force takes less energy required for working.

Comparing the rolling of carbon steel as shown in Figure 1, it is suggested that ST was more effective for rolling of stainless steel than carbon steel. In rolling of carbon steel as follows, where no seizure had occurred, only 7% reduction in rolling force was achieved by adding calcium carbonate.

Fig. 2 Roll surface after rolling tests in stainless steel
Left:ST0, Right:ST60

Fig. 3 Effects of calcium carbonate on thickness of rolled stainless strip

Fig. 4 Rolling force in stainless steel

Fig. 5 Effects of calcium carbonate content on the ratio of rolling force to rolling reduction

3.4. Analysis of rolled strip surface

The surfaces of stainless steel strips lubricated with ST30 and FT30 were analyzed after rolling to study the lubricating film structure.

First, the film structure was examined by EPMA. Figure 6 shows the EPMA images of each strip surface. ST30 and FT30 strips had only a few percent of Ca. Since EMPA is designed to detect the chemical composition of surface layers to a depth of 1 μm , the calcium film seemed to be thin.

Second, TOF-SIMS analysis was performed to study the film structure of the top surface. The strip surface was ion-etched to remove organic contaminants and four positions on the surface with several millimeters in distance were analyzed. Figure 7 shows the ion images of total, Ca^+ and Fe^+ in the area of $180 \times 180 \mu\text{m}$. ST30 and FT30 strips had Ca^+ clearly, indicating the presence of Ca film. Comparing the images of Ca^+ and Fe^+ , their distributions were not corresponding to each other. This means that the film consists of a mixture of the two components.

Consequently, XPS analysis was performed to study the nano-order film structure. The chemical composition was summarized in Table 4, which shows that ST30 strip contained more Ca, calcium content is estimated as the ratio of $\text{Ca}2\text{p}$ to $\text{Fe}2\text{p}$, than FT30 strips. In addition, a tribo-film mainly consisting of Ca was measured with ST30 at a depth of around 1nm after etching. In other words, the strip surface lubricated with ST was covered with a thicker tribo-film than that with FT. XPS spectra of $\text{Ca}2\text{p}$ and $\text{O}1\text{s}$ also revealed that the main component of the tribo-film was not calcium carbonate but calcium oxide.

TOF-SIMS analysis identified the film structure of the top surface layer and the XPS analysis confirmed that the Ca film of several nm was formed with ST. ST30 and FT30 strips had lubricating films of different thickness although both lubricants contain the same amount of calcium carbonate. The lubrication mechanism is schematically demonstrated in Figure 8 to

Fig. 6 EPMA images

Fig. 7 TOF-SIMS ion images ($180 \times 180 \mu\text{m}$)

Table 4 Chemical composition of tribo-films analyzed by XPS

Etching (3kV 6×6)	ST30 (Ca2p/Fe2p)	FT30 (Ca2p/Fe2p)
0 sec	3.9	0.9
15 sec (0.2 nm)	2.8	0.7
67 sec (1 nm)	1.9	0.6

Fig. 8 Lubrication mechanism at the contact of roll / strip with ST(a) and FT(b)

understand the difference between ST and FT.

A diameter of the calcium carbonate powder in ST was approximately $1\mu\text{m}$ whereas that of OBCS in FT was approximately 15 nm . The surface roughness of the roll used in rolling tests was approximately $1\mu\text{m}$ (Ra) and of the same order of magnitude as the diameter of the calcium carbonate powder in ST. With these in mind, it should be considered that the calcium carbonate powders were trapped in the surface asperity and aggregated at points of contact leading to less frequent surface contact. OBCS in FT was too small to be trapped and did not prevent surface contact. Thus, matching the diameter of calcium carbonate powders in a lubricant to roll surface roughness can facilitate the effective lubrication.

4. Application to actual hot strip mill

Considering all of the above results, the semi-fluid type lubricant with calcium carbonate powder dispersed in grease was evaluated in field trials using stainless angle steel in a hot rolling mill. Figure 9 shows the rolled strip surface. ST improved the surface quality greatly, whereas with a conventional hot rolling oil with a sulfur-containing EP additive, the strip had a poor quality surface and seizure occurred at the edge of the strip. ST showed better surface quality even without the sulfur-containing EP additive.

In general, the important component of hot rolling oil for stainless steel is a sulfur-containing EP additive. Seizure of stainless steel can be prevented with the oil containing a higher concentration of the EP additive. However, the environment should be contaminated by gases evolved from the additive during hot rolling. Here, the newly developed lubricant, ST exhibited better lubricating performance than a conventional lubricant

and prevented seizure without sulfur-containing EP additives in hot rolling of stainless steel.

The semi-fluid type lubricant has been used with success in five shape rolling mills in Japan, and is expected to be used in more mills.

5. Conclusions

Dispersion-type lubricants formulated with calcium carbonate were experimentally studied to achieve improved hot rolling characteristics of stainless steel. Conclusions from the measurements of hot rolling characteristics of OBCS-dispersed oil (FT) and calcium carbonate powder-dispersed grease (ST) are as follows:

- (1) ST greatly prevented seizure of stainless steel in hot rolling even without a sulfur-containing EP additive.
- (2) Calcium carbonate having a diameter of $1\mu\text{m}$, which was dispersed in grease was more effective than OBCS of a several tens nm diameter in preventing seizure.
- (3) With an increase in calcium carbonate content, ST exhibited more favorable lubricity and reduced the rolling force as well as the thickness of rolled strips.
- (4) Calcium carbonate prevented adhesion of the workpiece material to the roll surface by forming a tribo-film mainly consisting of calcium oxide.

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Fig. 9 Surface observation of stainless steel strips rolled with ST(a) and conventional hot rolling oil(b)

7. References

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