Study of Oiliness Agent for Cold Rolling Oil of Copper and Copper Alloy

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ABSTRACT Oil for the cold rolling of copper and copper alloys is generally a commercial rolling oil consisting of a low-viscosity mineral oil to which fatty alcohol and fatty acid ester is added as an oiliness agent. Because knowledge of the influence of oiliness agent on rolling performance and of how to maintain the rolling oil is considered by each company to be proprietary, there are few reports concerning cold rolling oils for copper and copper alloys. Thus typical copper alloys have been evaluated for an experimental rolling mill using commercial rolling oil. It has been understood that there is a problem in the lubricity of brass (Cu-Zn alloy) when rolled with commercial rolling oil. To study the oiliness agent in the rolling oil, the adsorption activity of a model oiliness agent component gas was evaluated, and acid and ether compounds were found to show the potential for enhancing the adsorption activity of the oiliness agent onto the nascent Cu-Zn alloy surface. In experimental rolling, it was confirmed that the lubrication performance of the oiliness agent added to standard oil could be improved by adding the ether compound without other problems. We also studied the type of ether compound and the proper amount of the ether compound, and examined to elucidate the lubrication mechanism by experimental rolling.

1. INTRODUCTION

Oil for the cold rolling of copper and copper alloys is generally a commercial rolling oil consisting of a low-viscosity mineral oil to which fatty alcohol and fatty acid ester is added as an oiliness agent. Because knowledge of the influence of oiliness agent on rolling performance and of how to maintain the rolling oil is considered by each company to be proprietary, there are few reports concerning cold rolling oils for copper and copper alloys. Pure copper (Cu), brass (Cu-Zn alloy) and phosphor bronze (Cu-Sn alloy) as three typical copper alloys were evaluated by step rolling in an experimental rolling mill using commercial rolling oil. It seemed that examination of an oiliness agent suitable for Cu-Zn alloy was necessary because the roll coating of the Cu-Zn alloy to the work-roll was remarkable, and a scaly pattern was observed on the rolled strip surfaces after rolling with commercial rolling oil. In order to select an oiliness agent suitable for Cu-Zn alloy, the adsorption characteristic of oiliness agents on a nascent Cu-Zn alloy surface was investigated and the values of adsorption activity were measured by experimental apparatus for adsorption tests. The ether compound and the fatty acid showed higher adsorption activity for Cu-Zn alloy.

Because subsequent discoloration was observed on the surface of strips after rolling with rolling oil containing fatty acid, we only studied use of the ether compounds. We also studied the type of ether compound and the proper amount of the ether compound by experimental rolling of Cu and Cu-Zn alloy. We also examined the reason why the ether compound was effective in increasing the rolling performance of Cu-Zn alloy.

2. EXPERIMENTAL

2.1 Rolling Tests with Commercial Rolling Oil

2.1.1 Test Conditions

The specifications and rolling conditions of the test mill are shown in Table 1.

For the material to be rolled, we selected 70%Cu-30%Zn alloy (C2600) as brass, Cu-8%Sn alloy (C5212) as phosphor bronze and tough pitch copper (C1100) as pure copper. We adopted a step rolling method, increasing reduction while rolling at a constant rate at regular intervals, and recorded the rolling data for each reduction. Rolling tension was constant because it could not be adjusted at each reduction. The rolling oil contained 15-% ester and about 1-% alcohol in a mineral oil of viscosity 4.6 mm^2/s as components. The work-roll roughness was

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Table 1 Test mill specifications and rolling conditions.

Test mill type	Reversing Z-High type mill
Work roll	ϕ51×220 mm (SKD-11) Surface roughness Ra=0.04 μm
Material	Copper (C1100) (t)0.3×(w)50 mm×coil Brass (C2600) (t)0.3×(w)50 mm×coil Bronze (C5212) (t)0.3×(w)50 mm×coil Buffing surface after full annealing
Rolling speed	70 m/min
Tension	Copper Entry: 815 N Exit: 490 N Brass Entry: 1360 N Exit: 1000 N Bronze Entry: 1360 N Exit: 1000 N
Rolling oil	Total volume 10 ℓ Flow rate 7 ℓ/min (Entry side) Temperature 40°C
Reduction	Copper 30, 40, 45, 50, 55, 60, 65, 70% Brass 20, 25, 30, 35, 40, 45, 50, 55% Bronze 20, 30, 40, 45, 50, 55, 60, 65% Rolling for 60 s at each reduction

Ra=0.04 μm and new rolling oil and a new work-roll was used for each material. Figure 1 shows the schematic of the experimental rolling mill.

2.1.2 Test Results
In the rolling tests we measured the rolling speed, the entrance and exit speed of the strip, the rolling load, the reduction, the front and back tension, and the temperature of the oil.

The relationship between the reduction and the rolling load for Cu, Cu-Zn alloy, and Cu-Sn alloy is shown in Figure 2.

The rolling load did not increase for Cu at a reduction of 50 % or more, even if the reduction increased, but when the rolling load increased for Cu-Zn alloy and Cu-Sn alloy as the reduction increased, and when reduction exceeded 45 % in Cu-Zn alloy, this tendency increased.

The strip surface photomicrograph of each material at 50-% reduction is shown in Figure 3. The transferred pattern of the work-roll and the oil pits could be observed on Cu and Cu-Sn alloy surfaces, but even at this reduction, we observed a scaly pattern that seemed to be a metallic adhesion of Cu-Zn alloy to the work roll, and when reduction exceeded 30 % it became remarkable. This seemed to be related with the fact that in the observation of roll coating after rolling, roll coating was not observed at all on the surface of the work roll for Cu and was observed clearly for Cu-Zn alloy. For Cu-Sn alloy roll coating was observed at a level midway between Cu and Cu-Zn alloy.

As shown by the above-mentioned result, the problem with rolling performance for Cu and Cu-Sn alloy was not seen using the commercial rolling oil, but there was a problem with Cu-Zn alloy in that there was thought to be an increase in rolling load by the adhesion of metal to the work-roll even under low reduction. Thus we aimed to improve rolling performance for Cu-Zn alloy. The oiliness agent was selected measuring the adsorption activity to the metal, considering that it was important that the oiliness agent be adsorbed to the rolling material or the work-roll.

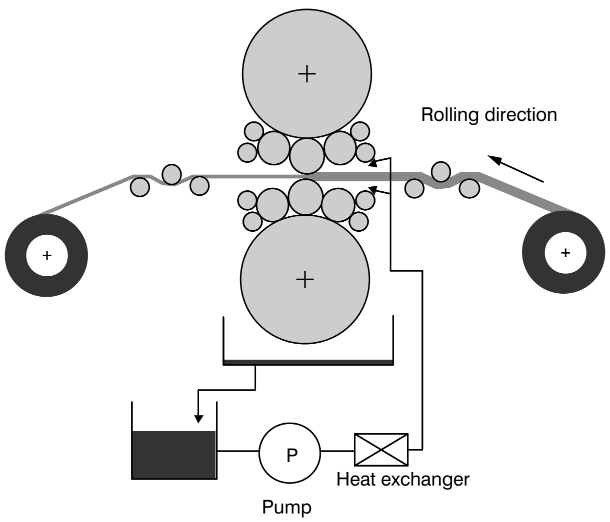


Figure 1 Z-high type test mill.

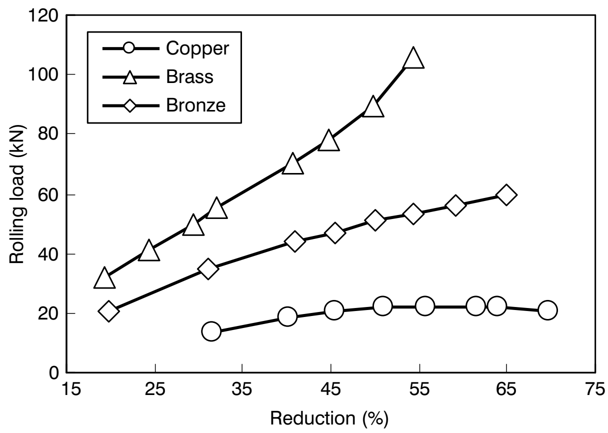


Figure 2 Relationship between rolling load and reduction.

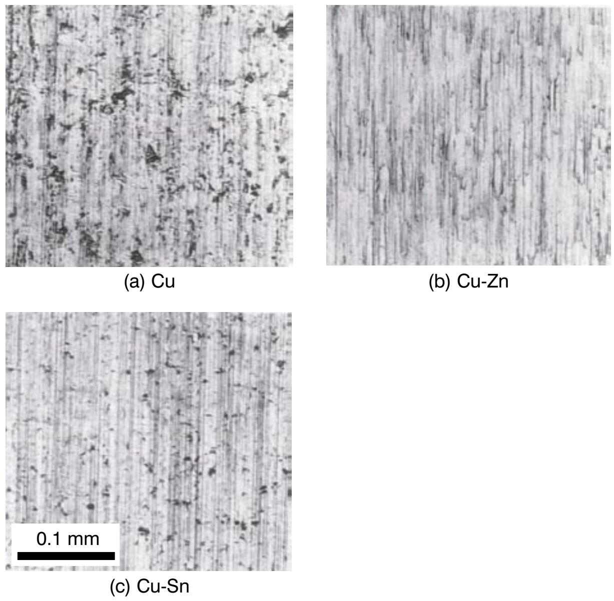


Figure 3 Microscopic observation of strip surface at 50% reduction.

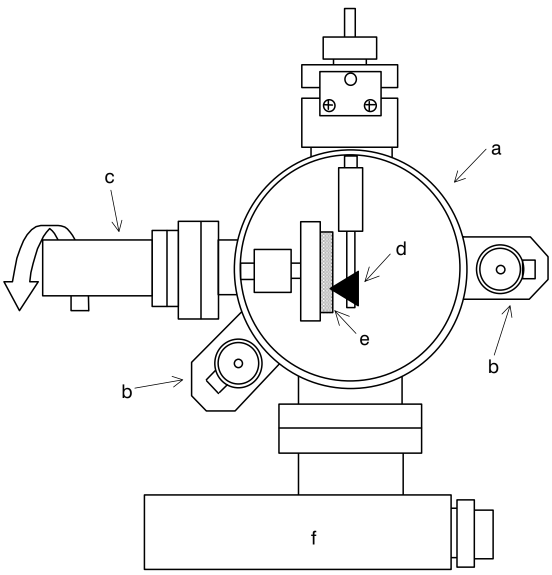
Table 2 Adsorption activity of model oiliness agents on the nascent surface of metal. (Adsorption activity, sec^{-1})

Model compounds of introduced gas	C1100 (0%Zn)	C2200 (10%Zn)	C2400 (20%Zn)	C2600 (30%Zn)	C2680 (35%Zn)	C2801 (40%Zn)	Zn
1-Butanol	0.07	0	0	0	0.03	0.04	0.02
Dibuthylether	0.05	0.05	0.08	0.04	0.06	0.08	0.07
Methylpropionate	0.10	0.04	0	0.05	0.02	0.04	0.03
Propionic acid	0.16	0.12	0.07	0.09	0.05	0.08	0.07

2.2 Measurement of Adsorption Activity

To examine the adsorption activity of the oiliness agent to the nascent Cu, Cu-Zn alloy and Zn surfaces, and to study the relationship to the rolling test result, adsorption activity was measured using the same apparatus used by Shibata for aluminum [1]. To confirm whether adsorption activity changes in proportion to the amount of zinc added to copper, a total of seven metals were investigated: pure copper, pure zinc, and five alloys of brass in actual use. The alloys tested are shown in Table 2. Figure 4 shows the experimental apparatus for the adsorption test. Because the oiliness agent does not have enough vapor pressure to be introduced in the apparatus, small molecular-weight and high vapor-pressure model gases of alcohol, ester, fatty acid, and ether were examined to represent the oiliness agent. The measurement result is also shown in Table 2.

These results showed that, while the adsorption activity of most kinds of the model gas to nascent metal surfaces was satisfactory for Cu, that for Cu-Zn alloy was near the adsorption activity for pure zinc and different from Cu, and Cu-Zn alloy having a Zn content of only 10 % showed different behavior from base metal, Cu. For zinc, dibutyl ether and propionic acid showed comparatively good adsorption activity, corresponding substantially to the results reported by Mori et al. [2].



a: Reaction chamber, b: Variable leak valves, c: Magnetic drive assembly, d: Cutting tool, e: Metal specimen, f: Mass spectrometer

Figure 4 Experimental apparatus for adsorption test.

Table 3 Test lubricants (I).

Oil No.	Viscosity @40°C (mm^2/s)	Butyl stearate (%)	Oleic acid (%)	Ether (%)
S1	10	5.2	—	—
S2	5.2	0.5	—	
S3	5.2	—	0.5	

As a result the rolling test was carried out using the oleic acid as the fatty acid and alkyleneglycol diol as the ether compound.

2.3 Rolling Tests to Consider Types of Oiliness Agent

The chemical composition of the oils tested is shown in Table 3. It was decided to add 0.5-% fatty acid and ether compound from the experience of aluminum rolling. The rolling conditions were the same as in Table 1, and Cu (C1100) and Cu-Zn alloy (C2600) were used as the rolled materials.

Figure 5 and Figure 6 show the relation between reduction and rolling load for Cu and Cu-Zn alloy using each of the oils tested.

It was a purpose in this rolling test to examine an additive suitable for use with the Cu-Zn alloy, but it is understood that a decrease in rolling load was seen from these results by adding the fatty acid and the ether compound effective for both Cu and Cu-Zn alloy, compared with the standard oil S1 which had only buthylstearate added.

Test oil S2 had 0.5-% fatty acid added and the test oil S3 had 0.5-% ether compound added to the standard oil.

The rolling load for test oils S2 and S3 was lower than for standard oil S1 at each reduction in the rolling of Cu. Moreover, the rolling load for test oil S2 showed a tendency to be higher than that of the standard oil S1 at low reduction of the Cu-Zn alloy, but rolling load decreased more than for the standard oil S1 at high reduction. Because the rolling load tendency for test oil S2 decreased more than for the standard oil S1 at high reduction, it was thought that the fatty acid achieved an effect under the severer rolling condition. Rolling loads lower than the standard oil S1 were shown under all reductions for test oil S3, the effect of a decrease in rolling load for test oil S3 was larger than for test oil S2, and the effect of test oil S3 was also admitted under a light reduction.

Strip surface photomicrographs at 55-% reduction of Cu-Zn alloy rolled with oils S1, S2, and S3 are shown in Figure 7. Heavily scaly patterns, which seemed to be due

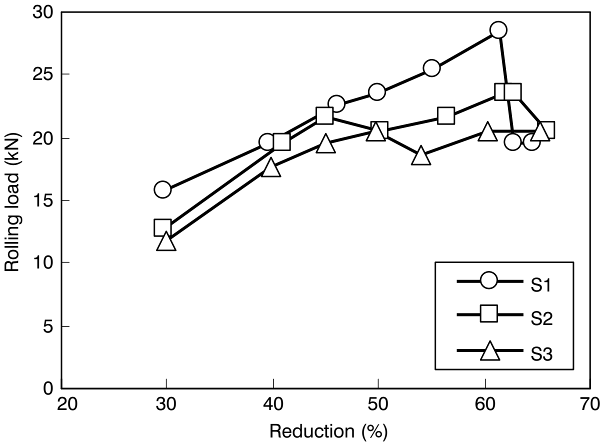


Figure 5 Relationship between rolling load and reduction for Cu (I).

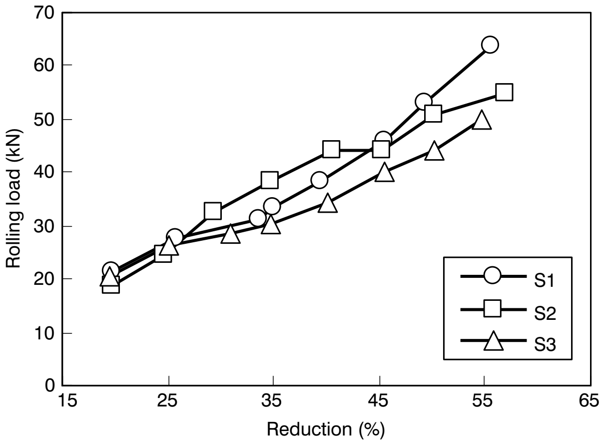


Figure 6 Relationship between rolling load and reduction for Cu-Zn alloy (I).

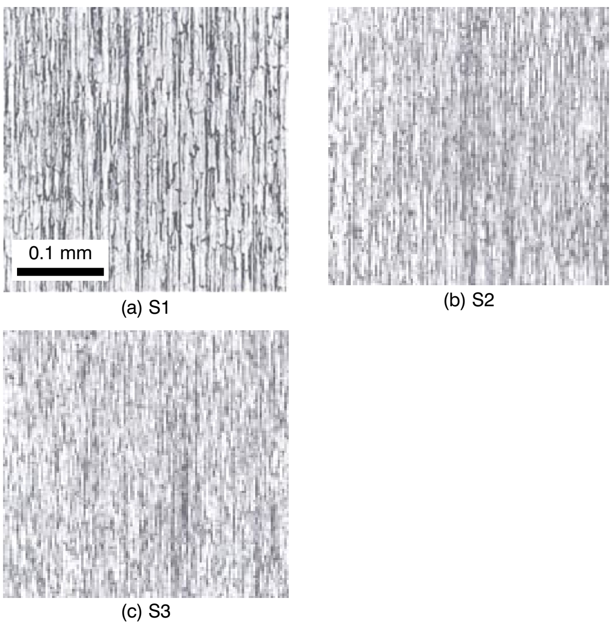


Figure 7 Microscopic observation of strip surface at 55% reduction for Cu-Zn alloy.

to the adhesion of metal to the work roll on the surface of strips rolled with standard oil S1, were observed to be as same as in the rolling test with commercial rolling oil. Scaly patterns weakened in test oil S2, and they were obviously small and weak on the surface of strips rolled with test oil S3. Partial oil pits were observed when using test oils S2 and S3. The reduction at which the scaly pattern appeared under microscopic observation on the surface of strips at each reduction was 30 % for standard oil S1 but 45 % for test oil S3.

It was confirmed that the fatty acid and the ether compound, which seemed to exhibit high adsorption activity to Cu-Zn alloy, were effective in improving rolling lubricity for Cu-Zn alloy, but it was found that the rolling load decrease was effective for both Cu-Zn alloy and Cu. With the rolling oil containing fatty acid, however, discoloration was observed on the surface of strips after subsequent rolling, so that we only studied use of ether compounds.

Therefore as the next step we investigated the type of ether compound.

2.4 Rolling Test for Selecting Type of Ether Compound

The chemical composition of the test oil is shown in Table 4. Each ether compound was added in the amount of 0.5 % using the same standard oil S1 as in the test on the type of oiliness agent. The rolling conditions were the same as in Table 1 and Cu (C1100) and Cu-Zn alloy (C2600) were used as the rolled work. Figure 8 and Figure 9 show the relation between the reduction and the rolling load for Cu and Cu-Zn alloy. When 0.5 % of the ether compound was added to standard oil S1 in Cu rolling from Figure 9, it was found that any kind of ether compound had an effect in decreasing the rolling load. The rolling load reduction effect was comparatively large for ester type test oils S2 and S3 and was larger for ether type test oil S5. For test oil S3 however, blue-green oil discoloration occurred after rolling and since this was similar to the discoloration that occurred with the addition of the fatty acid in the previous experiment, it is thought that non-esterified fatty acid was present. The change in rolling load at reduction of 40 % or less was relatively small among test oils for Cu-Zn alloy in Figure 9, but when the reduction exceeded 45 % it was large.

Table 4 Test lubricants (II).

No.	Content
S1	Base oil+Butylstearate 10 mass% (Standard)
S2	S1+Alkyleneglycol monooleate 0.5 mass%
S3	S1+Alkyleneglycol diester 0.5 mass%
S4	S1+Alkyleneglycol monoether 0.5 mass%
S5	S1+Alkyleneglycol monolaurylether 0.5 mass%
S6	S1+Alkyleneglycol diol 0.5 mass%
S7	S1+Alkyleneglycol monoglycerilether 0.5 mass%

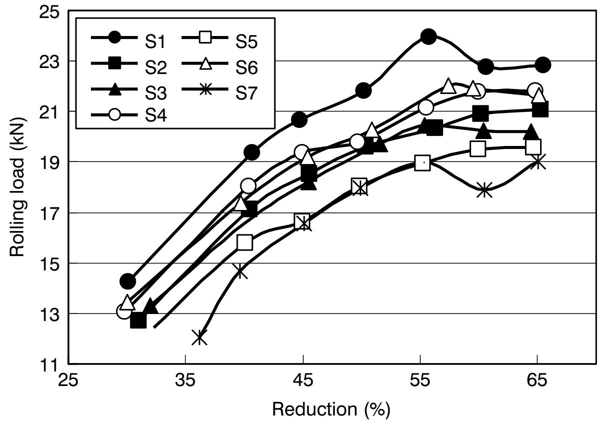


Figure 8 Relationship between rolling load and reduction for Cu (Ⅱ).

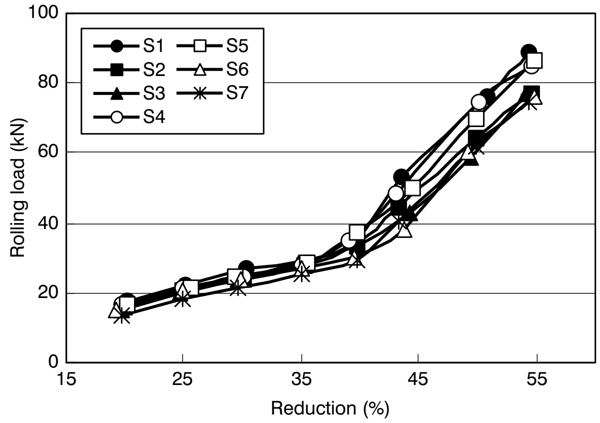


Figure 9 Relationship between rolling load and reduction for Cu-Zn alloy (Ⅱ).

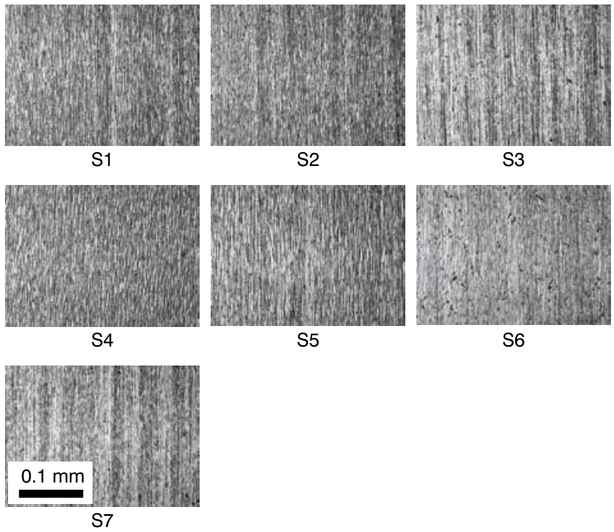


Figure 10 Microscopic photograph of strip surface at 45% reduction for Cu-Zn alloy, x180 (Ⅰ).

Table 5 Test lubricants (Ⅲ).

Oil No.	Base oil (mm²/s @40°C)	Butyl-stearate (wt%)	Alkylene-glycol monooleate (wt%)	Alkylene-glycol diol (wt%)
S1	5.2	10.0	0.0	0.0
S2-1	5.2	10.0	0.25	0.0
S2-2	5.2	10.0	1.0	0.0
S2-3	5.2	10.0	3.0	0.0
S6-1	5.2	10.0	0.0	0.25
S6-2	5.2	10.0	0.0	1.0
S6-3	5.2	10.0	0.0	3.0

In Figure 10 a scaly pattern was observed on the surface of Cu-Zn alloy with standard oil S1, test oil S2, test oil S4, and test oil S5, but transferred patterns of the work roll and oil pits were observed with test oil S3, test oil S6 and test oil S7. A larger number of oil pits were observed on the surface of Cu-Zn alloy with test oil S6, and virtually no scaly pattern was seen.

2.5 Examination of Amount of Ether Compound Added

Despite the fact that the amount added was only 0.5 %, the ether compounds evaluated in Section 2.4 were effective in decreasing the rolling load for Cu-Zn alloy with the standard oil. This effect was also shown in decreasing the rolling load for Cu. To determine the proper amount of ether compound to be added, we varied the amount of alkyleneglycol diol, which in the previous experiment had a large effect in decreasing rolling load, and alkyleneglycol monooleate, which had an intermediate effect, and the effect was examined. The rolling test conditions were the same as in the previous experiment. As in the previous experiment a mineral oil with viscosity of 5.2 mm²/s at 40℃ was used as the base oil, and an oil with 10-% buthylstearate added was used as standard oil S1. The composition of test oils is shown in Table 5.

The relationship between reduction and rolling load for Cu when alkyleneglycol monooleate and alkyleneglycol diol were added changing the concentration is shown in Figure 11 and the relationship for Cu-Zn alloy is shown in Figure 12.

From Figure 11 we see that for Cu the rolling load decreased with test oil S2-1 which has 0.25-% alkyleneglycol monooleate added compared to standard oil S1. The same tendency was shown for test oils S2-2 and S2-3. Even for test oils S6-1, S6-2 and S6-3, with added alkyleneglycol diol, the decrease in rolling load was the same as for test oil S2. In particular for test oil S6-3 the rolling load decreased at all reduction ratios by 20~25 % compared with standard oil S1.

For Cu-Zn alloy in Figure 12, the decrease in rolling load for test oils S2-1, S2-2 and S2-3 with alkyleneglycol monooleate added and test oils S6-1, S6-2 and 6-3 with alkyleneglycol diol added was no larger than for standard oil S1 at reductions 40 % or less, but a large decrease in rolling load was seen at reductions of 40 % or more compared with standard oil S1. Moreover, there was a tendency with test oils S2 and S6 that the rolling load did not increase in the high-reduction range the larger the added amount of the additives.

Figure 13 shows the photomicrograph of Cu-Zn alloy after rolling. The strip surface of Cu-Zn alloy showed a completely scaly pattern with standard oil S1 at 45-%

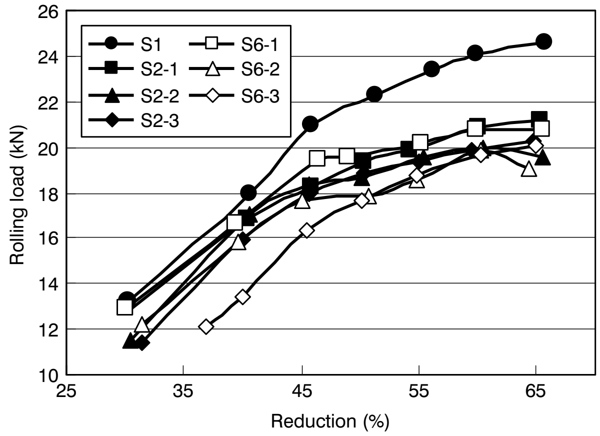


Figure 11 Relationship between rolling load and reduction for Cu (Ⅲ).

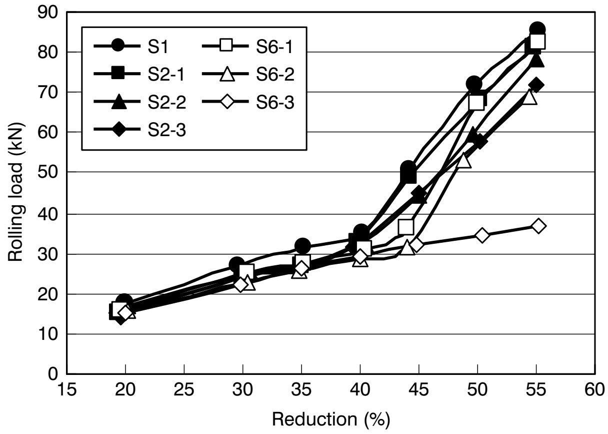


Figure 12 Relationship between rolling load and reduction for Cu-Zn alloy (Ⅲ).

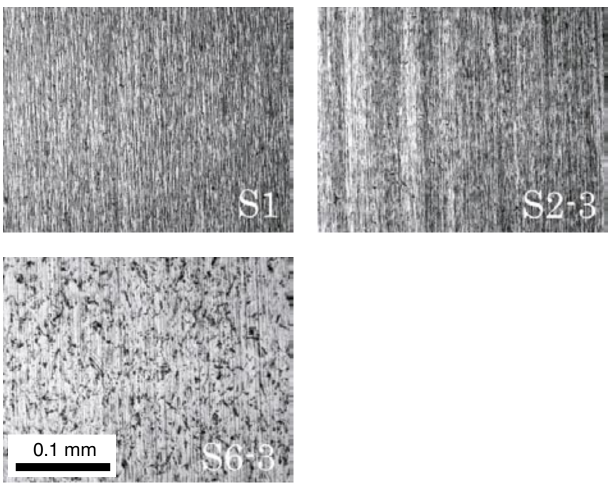


Figure 13 Microscopic photograph of strip surface at 45% reduction for Cu-Zn alloy, x180 (Ⅱ).

reduction, but only a weak scaly pattern with a certain amount of oil pitting with test oil S2-3, and oil pitting only with no scaly pattern for test oil S6-3.

Figure 14 shows photomicrograph of the work roll surface after rolling of Cu-Zn alloy. Metal adhesion to the work roll surface was observed after the rolling of Cu-Zn alloy using standard oil S1 and test oil S2-3. However little

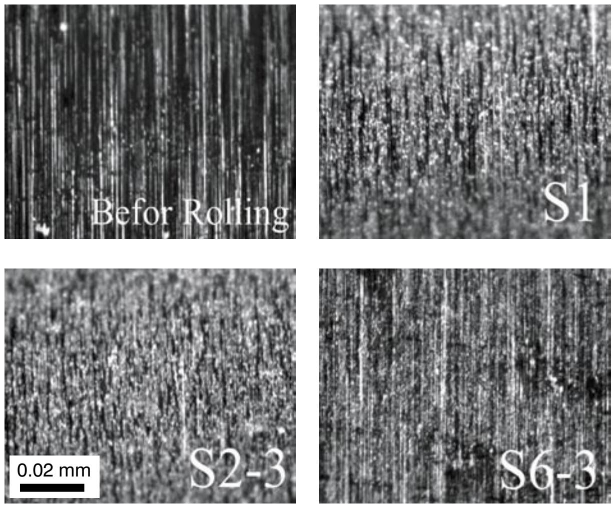


Figure 14 Microscopic photograph of roll surface after rolling for Cu-Zn alloy, x600.

metal adhesion was observed on the work roll after Cu-Zn alloy rolling with test oil S6-3, and this may be attributable to the large decrease in rolling load with test oil S6-3.

2.6 Rolling Tests to Confirm Lubrication Mechanism

The roll coating for Cu-Zn alloy was limited, and an oiliness agent that decreased rolling load was found. This oiliness agent has the ether bonds in its molecules, and it is supposed that this portion has the property of adsorbing strongly to copper-based materials. However, because the mechanism by which the ether compound contributes to lubricating in the rolling of copper-based materials is unclear, further examination was carried out by rolling tests.

The rolling conditions were in accordance with Table 1, and only Cu-Zn alloy was rolled at a constant reduction of 45 %. The standard oil was mineral oil of viscosity 5.2 mm^2/s at 40°C with 10-% buthylstearate added and the concentration of alkyleneglycol diol was varied. The chemical composition of the test oils is shown in Table 6.

Figure 15 shows a comparison of rolling loads. All test oils with alkyleneglycol diol added showed rolling loads lower than the standard oil, and the effect on the amount added became substantially constant at 2.0 % or more.

Figure 16 shows a comparison of amount of wear debris produced. Wear debris when alkyleneglycol diol was not added was greater than when it was. A larger difference was seen in the amount of wear debris adhering to the strip than in the amount of wear debris in the oil. The amount of wear debris produced when alkyleneglycol diol was added was substantially the same irrespective of the concentration of alkyleneglycol diol in the test oil, and no effect was found due to alkyleneglycol diol concentration in the range of this examination.

Table 6 Composition of oiliness agents (mass %).

Coolant No.	1	2	3	4	5
Butyl stearate	10	10	10	10	10
Ether	0	0.5	1.0	2.0	3.0

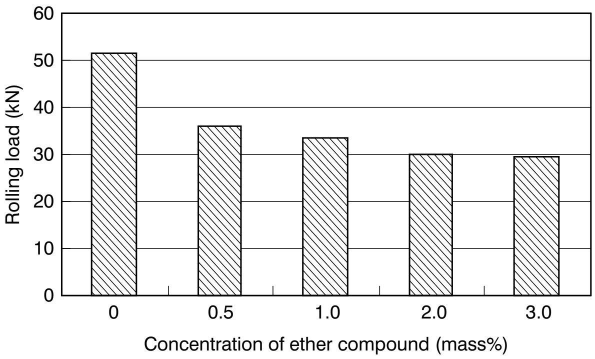


Figure 15 Relationship between ether concentration and rolling load.

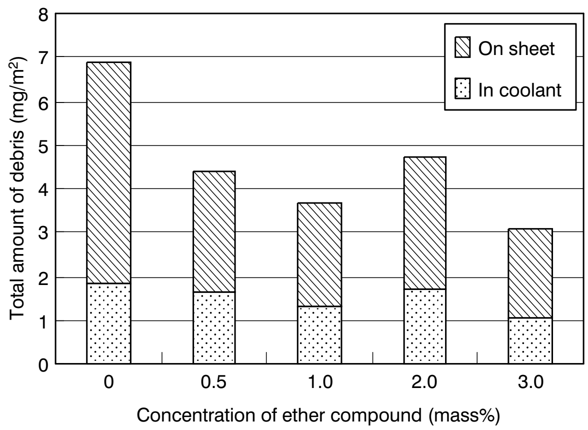


Figure 16 Relationship between ether concentration and total amount of debris.

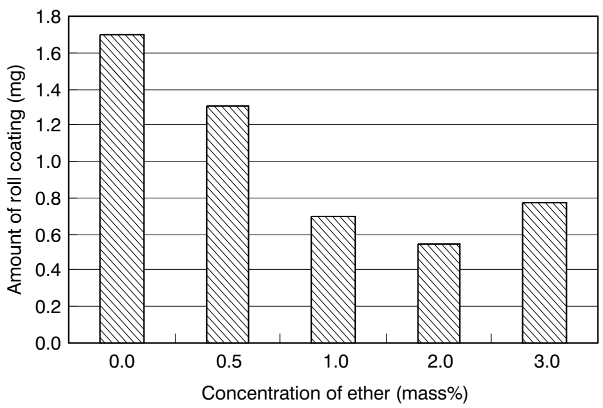


Figure 17 Relationship between ether concentration and amount of roll coating.

The amounts of roll coating after the rolling test were compared, and are shown in Figure 17. The amount of roll coating decreased with the addition of alkyleneglycol diol, and showed a constant value by adding approximately 1.0 %. Because the roll coating was due to adhesion of the rolled metal to the work-roll and the amount decreased, it is thought that alkyleneglycol diol had the effect of preventing adhesion during rolling. It is thought that the decrease in the amount of wear debris was due to the prevention of metal adhesion and it is of interest

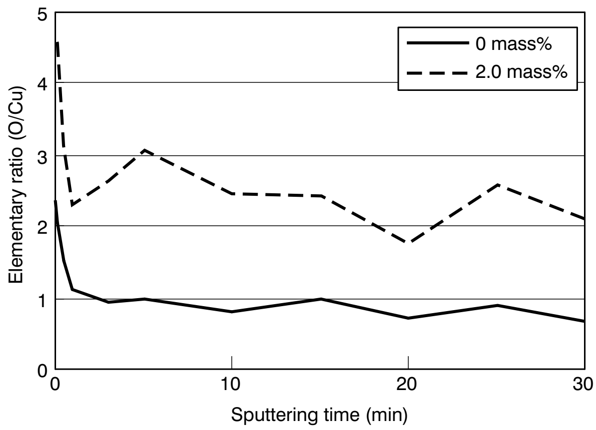


Figure 18 Relationship between sputtering time and O/Cu elementary ratio by XPS.

that the ratio of the amount of debris in the oil to the amount adhering to the strip was changed by the addition of alkyleneglycol diol.

The chemical composition of the roll coating was measured by using X-ray photoelectron spectroscopy. The ratio of oxygen to copper (O/Cu) was determined and is shown in Figure 18. Roll coating became richer in oxygen content by the addition of alkyleneglycol diol. It has not yet been possible to verify whether this oxygen was from the atmosphere or from the ether compound, but at any rate it is thought that the nascent metal surface produced by rolling was effectively oxidized and adhesion was prevented.

3. SUMMARY

- Rolling load, the amount of wear debris, and the amount of the roll coating were decreased by the addition of ether compound.
- It is thought that the addition of ether compound limits the adhesion of Cu-Zn alloy to the work-roll.
- Lubricity can be improved by ether compound not only for Cu-Zn alloy but also for Cu.

It is postulated that the limiting of the above-mentioned adhesion is due to the effective oxidation of the nascent metal surface produced by rolling.

A problem for future consideration is to collect data on whether the condition of the strip surface and other characteristics of the rolled product are changed by the addition of ether compound.

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