# **Temperature Dependencies of the Tribological Properties of Copper-Molybdenum Binary Oxide Powders**

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## Summary

Aluminum bronze coated with  $MoO_3$  powder was rubbed against stainless steel in our previous work and it was suggested that copper molybdate was generated on the friction track at high temperature and acted as high temperature lubricant. Thus, in order to investigate the lubricity of copper molybdate powders, the lubricating properties of  $MoO_3$ , CuO and two kinds of copper molybdate (Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and CuMoO<sub>4</sub>) powders supplied to the sliding interface of stainless steel specimens were studied under various temperature conditions up to 700 °C. Copper molybdate powders were synthesized by heating the mixture of MoO<sub>3</sub> and CuO powders in air under certain temperature conditions. Both of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and CuMoO<sub>4</sub> powders showed lower friction coefficient with increasing of ambient temperature. On the other hand, at high temperatures, MoO<sub>3</sub> and CuO powders showed poor lubricity and they showed higher wear amount of stainless steel specimens comparing with two types of copper molybdate powders. It was suggested that the good adhesiveness of copper molybdate powder on the stainless steel at high temperature could be one of the reasons of excellent lubricating properties of them.

#### 1. Introduction

We have studied tribological properties of aluminum bronze which is one of the conventional sliding bearing [1]. In our previous work, we studied the effects of molybdenum trioxide (MoO<sub>3</sub>) on the friction and wear properties of aluminum bronze under high temperature conditions up to 700 °C [2]. MoO<sub>3</sub> powder was coated on the sliding surface of ring-shaped stainless steel counterpart specimen. The friction coefficient for the MoO<sub>3</sub> coated specimen was lower than that of uncoated specimen at high temperature of over 500 °C. Besides, MoO<sub>3</sub> powder coating drastically decreased the wear amounts of aluminum bronze and stainless steel counterpart at high temperature.

As a result of observation and analysis of the friction track, it was revealed that small quantity of copper-molybdenum oxide composite (copper molybdate) was generated on the friction track during sliding at high temperature and this generated material was considered as  $Cu_3Mo_2O_9$  through X-ray diffraction

pattern matching.

The lubricity of many kinds of metal oxide at high temperature has been studied. It was reported that MoO<sub>3</sub> showed superior lubricity at high temperature of about 700 °C [3]. In the case of friction between aluminum bronze and stainless steel, however, it was considered that MoO<sub>3</sub> doesn't work directly as a lubricant at high temperature but it reduced friction and wear by changing into Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>. Copper contained in the aluminum bronze is easily oxidized especially at the surface by heating in air. Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> was generated during sliding at high temperature under high pressure by the reaction of MoO<sub>3</sub> powder and copper oxide (CuO). Wahl et al. reported that the ion-beam deposited amorphous Cu-Mo coating on alumina substrates showed low friction coefficient at 530 and 650 °C [4]. They suggested that the amorphous Cu-Mo coating changed to crystalline oxide and that the softened oxides worked as high temperature lubricant. This crystalline oxide was referred to as CuMoO<sub>4</sub> for simplicity.

The generated material in our experiment Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>

is one of the several kinds of copper molybdates and it is possible that  $Cu_3Mo_2O_9$  which has similar ingredient with  $CuMoO_4$  is softened and shows superior lubricity at high temperature. In order to investigate the lubricity of this copper molybdate, we studied lubrication properties of two kinds of copper molybdate powders ( $CuMoO_4$  and  $Cu_3Mo_2O_9$ ) and two kinds of single-metal oxide powders ( $MoO_3$  and CuO) supplied between the stainless steel surfaces.

## 2. Experiment

# 2.1 Sample preparation

 $MoO_3$  and CuO powders are commercially available.  $Cu_3Mo_2O_9$  and  $CuMoO_4$  powders were synthesized by heating the mixture of  $MoO_3$  and CuO powders in the electric furnace at 700 °C for 1 h and 500 °C for 120 h, respectively. These heating conditions were decided as the result of trial and error. Figure 1(a) and 1(c) show the XRD spectra obtained from the synthesized  $Cu_3Mo_2O_9$  and  $CuMoO_4$  powders, respectively. These spectra were obtained by using X-ray from cobalt target. For the identification of these synthesized powders, the



Fig. 1 XRD spectra obtained from synthesized (a) Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and (c) CuMoO<sub>4</sub>, reference peak intensity of (b) Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and (d) CuMoO<sub>4</sub> in the database, and XRD spectrum obtained from the friction track of aluminum bronze rubbed against MoO<sub>3</sub> powder coated stainless steel specimen at 600 °C.

diffraction peak intensities of  $Cu_3Mo_2O_9$  and  $CuMoO_4$ in the database for the copper target X-ray source are also shown in Fig. 1(b) and 1(d), respectively. Taking into account the difference between the wavelength of X-ray from cobalt target and that from copper target, the diffraction angles of the reference data were shifted in this figure. Both of the XRD spectra obtained from the synthesized powders showed good agreement with the reference data. The XRD spectrum obtained from the friction track of aluminum alloy coated with  $MoO_3$ tested at 600 °C is shown in the Fig. 1(e) for comparison.

Stainless steel, SUS304 (JIS G 4303) was tested as a disk and ring specimens. The sliding surface of ring specimen was slightly sandblasted with the alumina abrasives, and then each oxide powder was accumulated on the blasted surface as a powder coating. The quantity of accumulated oxide powder on the specimen was estimated by measuring the weight of specimen before and after coating treatment, and was controlled to be between 5 and 7 mg.

#### 2.2 Friction test

The friction test was conducted with the ring-on-disk tribometer with a furnace in which the ring and disk specimens were mounted (Figure 2). The outer and inner diameter of the ring specimen was 20 and 15 mm, respectively. The thickness of disk specimen was 5 mm. The applied load was 61.8 N which corresponds to the contact pressure of 0.46 MPa. The rotating speed of the ring specimen was 60 rpm which corresponds to the sliding speed of 55 mm/s. The sliding distance was about 200 m. The temperature in the furnace was controlled to be from the room temperature (R.T.) to



Fig.2 Tribometer with a furnace used in this experiment.

700 °C. The wear amount of the specimen was obtained as a weight loss by measuring the weight of the specimen before and after friction test. Preliminary to the friction test, it was confirmed that the weight increase of heated specimen by oxidation was negligibly small comparing with the value of wear amount.

## 3. Results and discussion

Friction coefficients of non-coated specimen and four kinds of oxide powder coated specimens at each atmospheric temperature are shown in Fig. 3(a). Figure 3(b) shows the wear amount of each ring specimen.

MoO<sub>3</sub>, Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and CuMoO<sub>4</sub> coated specimens showed higher friction coefficient comparing with non-coated specimen at room temperature. There was little difference in friction coefficient among all specimens at the temperature from 200 to 500 °C. Both of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> and CuMoO<sub>4</sub> coated specimens showed lower friction coefficient than other specimens at the temperature of over 500 °C. Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> coated specimen showed the lowest friction coefficient of 0.32 at 700 °C. On the other hand, MoO<sub>3</sub> and CuO showed poor lubricating ability at the temperature of over 500 °C.

Powder coatings were not effective to reduce wear amount of stainless steel specimens at the temperature from 200 to 500 °C. On the other hand, wear amount of  $Cu_3Mo_2O_9$  and  $CuMoO_4$  coated specimens at 600 and 700 °C were quite small comparing with that of  $MoO_3$  and CuO coated specimens.

Figure 4 shows EPMA spectra obtained from the



Fig. 3 (a) Friction coefficient and (b) wear amount of ring specimen at each temperature.

friction track of the Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> coated ring specimens tested at (a) 400 °C and (b) 700 °C. X-ray peaks of Cu and Mo, which are constituent element of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, were not detected from the specimen tested at 400 °C. At this temperature, Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder coating was not effective to reduce the wear of specimens. On the contrary, the strong peaks of Cu and Mo were detected from the specimen tested at 700 °C, and Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder coating reduced friction coefficient and substantially reduced wear of the stainless steel specimens at this temperature. This means that adequate quantity of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> was remained during friction test at 700 °C, on the contrary, Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder was easily removed from friction track at 400 °C.

In order to considering this result, we heated small



Fig. 4 EPMA spectra obtained from the friction track of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> coated ring specimens tested at (a) 400 °C and (b) 700 °C.



Fig. 5 SEM images of the (a) synthesized Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> particles and (b) Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> particles heated on the stainless steel plate at 700 °C for 3 h in air.



Fig. 6 X-ray images of (a) Mo and (b) Cu obtained from the same observation area in Fig. 5(b).

quantity of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder on the stainless steel plate at 700 °C for 3 h in air. Figure 5(a) and 5(b) show the SEM images of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder before and after heating, respectively. SEM image of Fig. 5(b) was obtained from the particles which directly contact with stainless steel plate. The figure of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> particles changed from rounded shape to angulated shape by heating treatment on the stainless steel. It suggests that  $Cu_3Mo_2O_9$  powder react with stainless steel. Figure 6(a) and 6(b) show the X-ray images of Mo and Cu obtained from the same observation area in Fig. 5(b). If most of the particles shown in Fig. 5(b) consist of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>, the X-ray of Mo and Cu must be detected all together from the same position. Actually, however, X-ray images of Mo and Cu showed quite different distribution and this means that Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> was decomposed and reacted with stainless steel under high temperature. Therefore small portion of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> powder could adhere tightly to the stainless steel by reacting with stainless steel.

Wahl et al. suggested that softening of  $CuMoO_4$  at high temperature reduced friction coefficient of Cu-Mo coating [4]. Erdemir concluded that oxides with high ionic potentials exhibit low shear strength and hence high lubricity and that, in the case of mixed oxides, one must select from oxides that exhibit large differences in ionic potential [5]. In our experiments, it is possible that  $Cu_3Mo_2O_9$  and  $CuMoO_4$  powder showed lubricity because of their low shear strength under high temperature conditions. Not only that, it is supposed that good adhesiveness of copper molybdate powder on the stainless steel at high temperature could be one of the reasons of excellent lubricating properties.

#### 4. Conclusions

The lubrication properties of two kinds of copper molybdate powders  $Cu_3Mo_2O_9$  and  $CuMoO_4$  and two kinds of single metal oxide powders  $MoO_3$  and CuOsupplied between the stainless steel sliding surfaces were studied under the temperatures from room temperature to 700 °C. Both of copper molybdate powders showed lower friction coefficient with increasing of ambient temperature. On the other hand,  $MoO_3$  and CuO powders showed poor lubricating ability and they showed higher wear amount of stainless steel specimens comparing with two kinds of copper molybdate powders. It was suggested that the good adhesiveness of copper molybdate powder on the stainless steel at high temperature could be one of the reasons of excellent lubricating properties of them.

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