Jurnal Tribologi 20 (2019) 26-38

MYTRIBOS Malaysian Tribology Society

Jurnal Tribologi

Website : jurnaltribologi.mytribos.org e-issn: 2289-7232

Fundamental study on functionality of synthetic sulfides: Evaluation of metal sulfides as solid lubricant

Shuhei Ishikawa*, Tomohiro Sato, Ken-ichi Saitoh, Masanori Takuma, Yoshimasa Takahashi

Department of Mechanical Engineering, Faculty of Engineering Science, Kansai University, JAPAN.
*Corresponding author: k611896@kansai-u.ac.jp

KEYWORD

Metal sulfide
Bronze
Dry friction
Solid lubricant
Sintering

ABSTRACT

Replacement of exhaustible and harmful resources used as solid lubricants is required for sliding elements such as plain bearings. In particular, the substitution of lead containing in the lead bronze is considered an urgent task. Therefore, in this study, attention was focused on metal sulfides (Cu_2S, Cu_5FeS_4, SnS, TiS_2, etc) as a substitute material for lead. After synthesis of sulfide and preparation of sintered body, friction and abrasion test was carried out and applicability as solid lubricant was investigated. The tribological properties of the dry conditions were evaluated by a journal type high speed tester. As a result, the friction coefficient of the bronze specimen without sulfide was about 0.3, whereas the bronze specimen containing sulfide showed a friction coefficient of about 0.1, indicating that the sulfide reduced the frictional resistance. Among them, the specimens containing Cu_2S and Cu_5FeS_4 exhibited a lower friction coefficient. It is considered that this is influenced not only by the effect of hardness but also by film formation by sulfide.

1.0 INTRODUCTION

Copper alloys are widely used as bearing alloys because they have low aggression to mating materials, excellent wear resistance, good heat conductivity and easy dissipation of friction generated heat. In particular, a lead bronze alloy in which lead is added as a solid lubricant to a bronze alloy (an alloy composed of copper and tin) is widely used from a driving part of a ship and a construction machine to a micro spindle motor for dental use. Lead is a very soft metal and

Received 29 June 2018; received in revised form 8 August 2018; accepted 23 August 2018.
To cite this article: Ishikawa et al. (2019). Fundamental study on functionality of synthetic sulfides: Evaluation of metal sulfides as solid lubricant. Jurnal Tribologi 20, pp.26-38.

easily plastically deforms, contributing to improvement of conformability to the shaft and improvement of seizure resistance. Lead also has good affinity with copper alloys and lubricating oils and has low melting point, so it plays a role of preventing damage of bearings due to heat generation accompanying sliding.

In recent years, however, the use of substances that adversely affect ecosystems is beginning to be prohibited due to the growing awareness of environmental conservation at the global level, and lead is also one of the substances whose use is restricted by RoHS and ELV regulations in Europe (Directive 2011/65/EU, 2011). Lead has an accumulation type of toxicity, it is said that once it is taken into the body it will deposit over a long period of time, causing symptoms in the nervous system such as fatigue and insomnia. According to the RoHS regulation, copper alloys are currently permitted to contain lead up to 4 mass%, but it is expected that these regulations will become more severe in the future. So, as a material that contributes to improvement of the frictional wear characteristics in place of lead, a soft metal type such as Bi(bismuth) or In(indium), a polymer type such as PTFE(polytetrafluoroethylene) or PI(polyimide), graphite or the like is studied (Nakayama et al., 2010, Kato et al., 2002, Tanizawa et al., 2012). However, bismuth and indium are rare metals, and it is difficult to substitute for lead in terms of cost. Also, polymeric materials such as PTFE have the disadvantage that the thermal stability in air is low. Although graphite is a very excellent lubricant, it also has disadvantages that it is easily affected by moisture (absolute humidity) in the atmosphere and loses its lubricity by oxidation at high temperatures.

Based on these facts, this study focuses on "sulfide" as a solid lubricant substituting for lead. Sulfides are not accumulation type toxicities like lead, they are rich in resources and many have lamellar structures as typified by MoS_2(Molybdenum disulfide), so they show a low coefficient of friction. Further, sulfide can be easily synthesized in a high purity state by mixing metal powder such as copper and tin with sulfur powder and heating in a vacuum state (Wada et al., 2004). Also, many sulfides have relatively high thermal stability. Currently, sulfide dispersed bronze containing Cu_5FeS_4 which is a copper-iron based sulfide in bronze powder has been developed (Sato et al., 2012, Hirai et al., 2016). It has been confirmed that the friction coefficient is reduced and seizure resistance is improved. Evaluation of frictional wear characteristics of bronze containing MoS_2 has also advanced (Kumar et al., 2013). However, the possibility of substitution with lead bronze including the detailed lubrication mechanism and strength of bronze containing sulfide has not been elucidated.

Therefore, in this research, in order to develop a sulfide bronze alloy which has high frictional wear characteristics which can be a substitute for lead bronze, from the synthesis process of various metal sulfides, uniform dispersion, sintering, frictional wear characteristics to bronze base, radial crash strength etc. are evaluated. In this report, friction and abrasion test was carried out on a sintered bronze alloy containing sulfide synthesized from metal powder and sulfur powder using a journal type high speed tester, and the tribological characteristics exerted by sulfide were investigated.

2.0 EXPERIMENTAL PROCEDURE

2.1 Sulfide synthesis

According to the stoichiometric ratio of the sulfide to be synthesized, metal powders and sulfur powders were weighed and mixed, vacuum sealed in an ampule tube, and heated in an electric furnace to synthesize sulfide. The types of sulfides synthesized as candidates for lead substitution in this study are copper sulfide (Ⅰ) Cu_2S, tin sulfide (Ⅱ) SnS, bornite Cu_5FeS_4, titanium sulfide (Ⅳ) TiS_2.These sulfides were selected because they can be expected to have a relatively low coefficient of friction, high thermal stability, abundant resources of metal powder as a raw material. Table 1 shows the powder used for synthesis. Synthesis temperature of sulfide is shown in Table 2 and synthesis time is shown in Table 3. As a comparison material, commercially available MoS_2 powder was also prepared and experimented.

Table 1 Powder properties.

Powder	**Element symbol**	**Particle size**
Copper	Cu	45 μm
Tin	Sn	
Iron	Fe	
Titanium	Ti	
Sulfur	S	105 μm
Molybdenum disulfide	MoS_2	3.5 μm

Table 2 Synthesis temperature.

Sulfide	**Temp. [°C]**	**Temp. [K]**
Cu_2S	200	473
Cu_5FeS_4		
SnS	350	623
TiS_2	500	773

Table 3 Synthesis time.

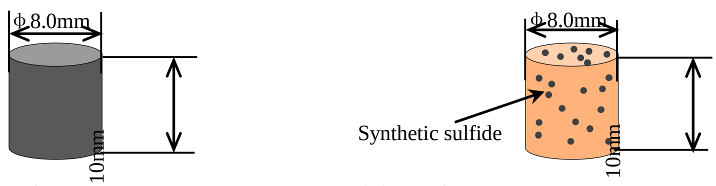
Process	**Time [hour]**
Heating	12
Holding	12
Cooling	6

2.2 Specimen preparation

Using the synthesized sulfides, the specimens used for the friction test were prepared. Two types of specimens were prepared: "Sulfide only specimen" obtained by sintering only synthesized sulfide and "Sulfide dispersed bronze specimen" sintered by adding sulfide to bronze powder. In the sulfide dispersed bronze test specimens, those having added amounts of synthesized sulfides of 1, 2, 5 and 10 mass% were prepared. The types of test specimens and test specimen fabrication conditions are shown in Table 4. A schematic diagram of the specimen is shown in Figure 1. The synthetic sulfide used for preparing the test piece was classified to 63 μm or less by using a classifier. For bronze powder, Nippon Atomized Metal Powders S91-325# (Sn: 8.79 mass%) was used.

Table 4 Specimen type.

Specimen	Molding Pressure	Sintering Temperature	Warm up Time	Sintering Time	Sintering Environment
Cu_2S Cu_5FeS_4 SnS TiS_2 MoS_2 Bronze Sulfide dispersed bronze (1,2,5,10 mass%)	250 MPa	923 K	20 min	40 min	Vacuum (0.2 Pa)



(a) Sulfide only specimen (b) Sulfide dispersed bronze specimen

Figure 1: Schematic diagram of specimen.

2.3 Friction and abrasion test

A friction and abrasion test was carried out on the prepared specimen by using a journal type high speed testing machine shown in the Figure 2. Lead bronze is frequently used as a journal bearing in high-speed sliding conditions in many cases, so by adopting this test method, it simulates an environment close to actual use. The load W and the friction force F are calculated from the deformation amount of the strain gauge attached to the position of ① to ⑧ of the octagonal ring shown in Figure 3 and the friction coefficient μ is obtained based on them. Carbon Steel (S45C/ Japan Industrial Standard, JIS) shaft of HV 600 was adopted as the mating material of the test specimen, and the test was carried out at room temperature drying condition without using lubricating oil. Table 5 shows friction test conditions. The amount of abrasion was calculated from changes in the mass of the specimen before and after the test and was measured only for " Sulfide only test specimen ".

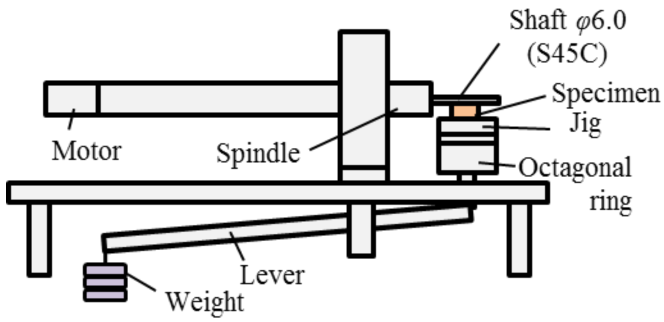


Figure 2: Schematic sketch of the testing apparatus.

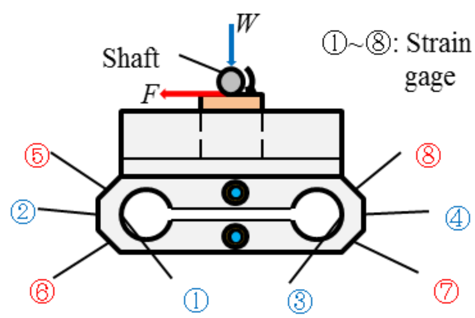


Figure 3: Octagonal ring.

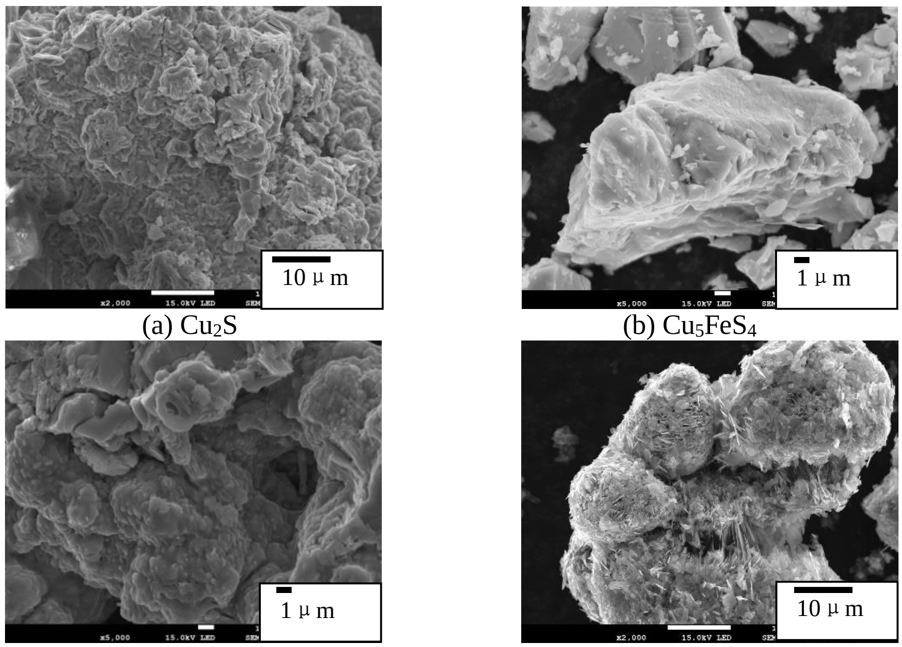
Table 5 Friction test conditions.

Environment	Dry
Test temperature	RT
Load	9 N, 0.88 MPa
Test time	300 s
Rotation speed	1.57 m/s (5,000 rpm)
Material of the shaft	S45C (No heat treatment); Ra: 0.06 μm

3.0 RESULTS AND DISCUSSION

3.1 Sulfide synthesis result

The scanning electron microscope (SEM) images of the synthesized sulfide powder are shown in Figure 4. The synthesis of each sulfide is confirmed by X-ray diffraction. From this, it can be seen that metal sulfides such as copper sulfide and titanium sulfide can be easily synthesized by a simple synthesis method that mixes metal powder as a raw material and sulfur powder and heating in vacuum. In addition, we obtained synthesized material like Figure 4 in this synthesis condition, but it was also confirmed that composition and orientation of the compound changed by controlling synthesis time, synthesis temperature, atmosphere. From this fact, it is possible that in the future, by changing the heat treatment process at the time of synthesis, it is possible to control the structure to an orientation with better slidability.



(a) Cu_2S (b) Cu_5FeS_4

(c) SnS (d) TiS_2

Figure 4: SEM image of synthetic sulfide powder.

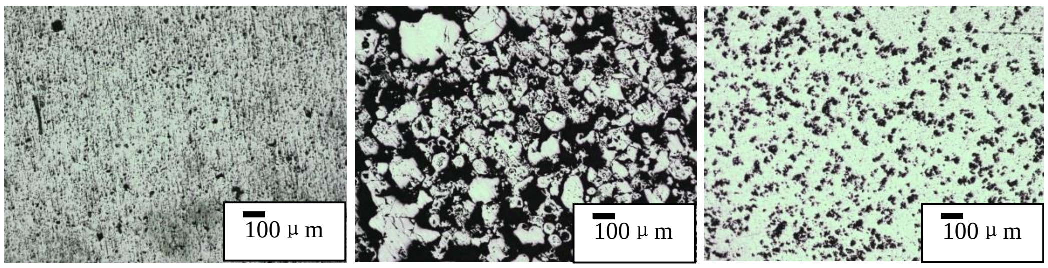
3.2 Results of specimen preparation

3.2.1 Sulfide only specimen

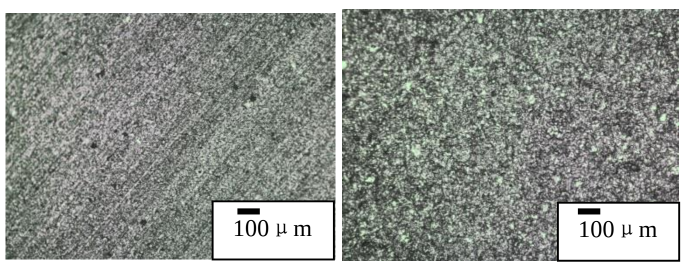
The optical micrographs of the surface of the sulfide only test specimen are shown in Figure 5. In these images, it looks black as pores, those with a large black portion mean that sintering is not progressing. From this, it can be seen that sintering of Cu_5FeS_4 is hardly progressed. Since the melting point of Cu_5FeS_4 is 1273 K or more, it is considered that the temperature was insufficient at this sintering temperature of 973 K. In this case, only the sulfide specimens were sintered at 973 K which is the temperature at which bronze is usually sintered. However, when sulfide is actually used as a solid lubricant, since it is dispersed in bronze, the sinterability of the sulfide is not considered to be important.

3.2.2 Sulfide dispersed bronze specimen

The optical micrographs of the surface of the specimen of sulfide dispersed bronze containing 2 mass% synthetic sulfides are shown in Figure 6. In these photographs, it can be seen that the substance which looks black is a sulfide, and the sulfide is not lost during the sintering process but remains in the bronze matrix and is dispersed. However, the dispersion state of the sulfide varies depending on the type of the sulfide, and it is understood that the test specimen added with SnS or MoS_2 is not uniformly dispersed on the surface. That is, wettability or affinity between sulfide and bronze is thought to differ depending on sulfide. In order to more uniformly disperse the sulfide in the future, it is considered important to study the particle size and shape of the powder, sintering conditions and so on.

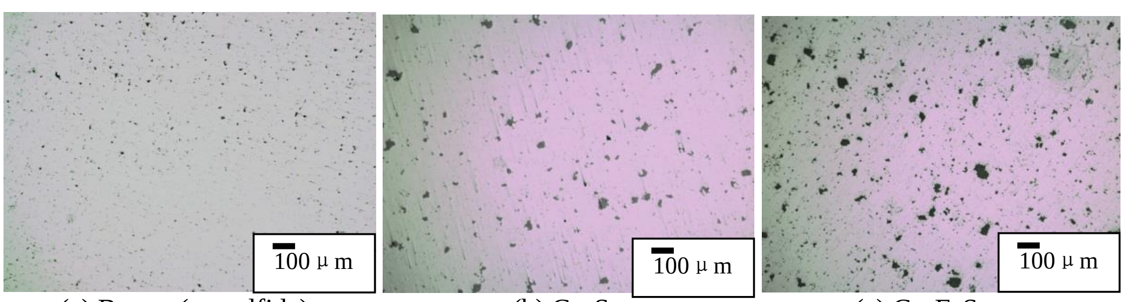


(a) Cu_2S (b) Cu_5FeS_4 (c) SnS

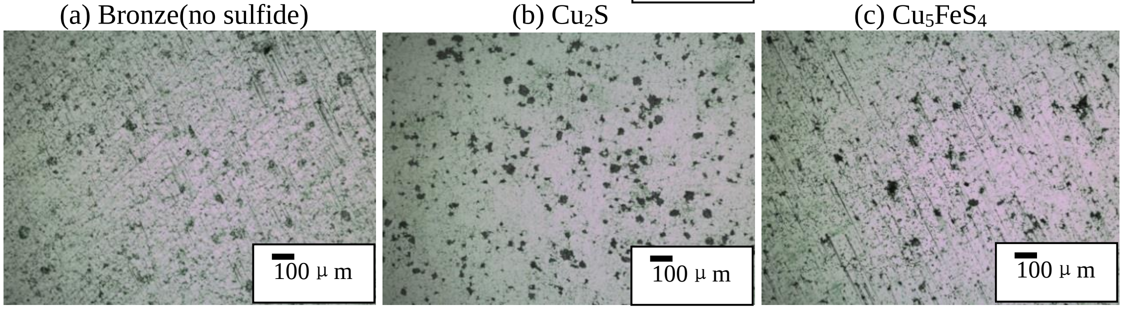


(d) TiS_2 (e) MoS_2

Figure 5: Optical micrograph of the specimen surface of the specimen only sulfide.



(a) Bronze(no sulfide) (b) Cu_2S (c) Cu_5FeS_4



(d) SnS (e) TiS_2 (f) MoS_2

Figure 6: Surface of specimen of sulfide dispersed bronze specimen (sulfide addition amount 2 mass%).

3.3 Friction test result

3.3.1 Sulfide only specimen

The results of the friction test of the sulfide only specimen are shown in Figure 7 and the results of abrasion and hardness are shown in Figure 8. Although the test time was set at 300 seconds, since the sintering was not progressed and the wear amount was excessive, the test was stopped in 60 seconds. From Figure 7, Cu_2S and TiS_2 have a relatively low coefficient of friction of about 0.3 to 0.35, indicating that there is a possibility of functioning as a good solid lubricant. On the other hand, Cu_5FeS_4 and SnS have been maintained with a friction coefficient of about 0.35 to 0.45, showing a somewhat higher value than the other sulfides. From the Figure 8, it can be seen that the amount of wear of Cu_5FeS_4 is prominent. This is probably because the sintering of Cu_5Fe_4 was scarcely advanced and the sliding state was close to cutting as mentioned above in the test piece production result. Furthermore, the Figure 8 shows that the Vickers hardness of Cu_2S was slightly larger than that of other sulfides, but the coefficient of friction was the second lowest value after MoS_2. In general, the coefficient of friction μ when the solids slide relative to each other is given by μ = S (shear strength at the sliding interface part) / H (hardness), so not the shear strength of the sulfide but the hardness may have influenced the friction test result.

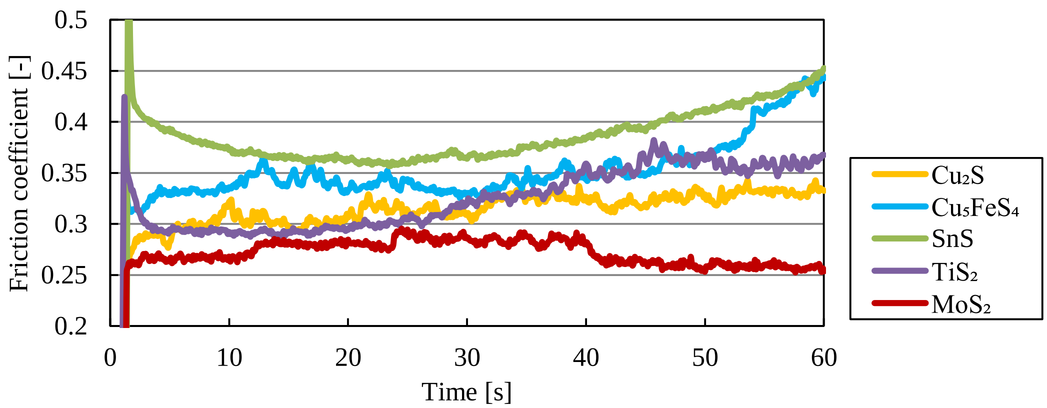


Figure 7: Friction coefficient (sulfide only specimen).

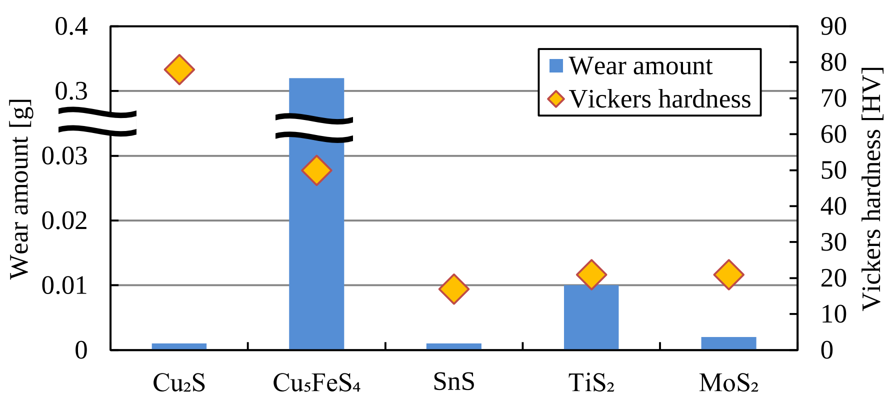
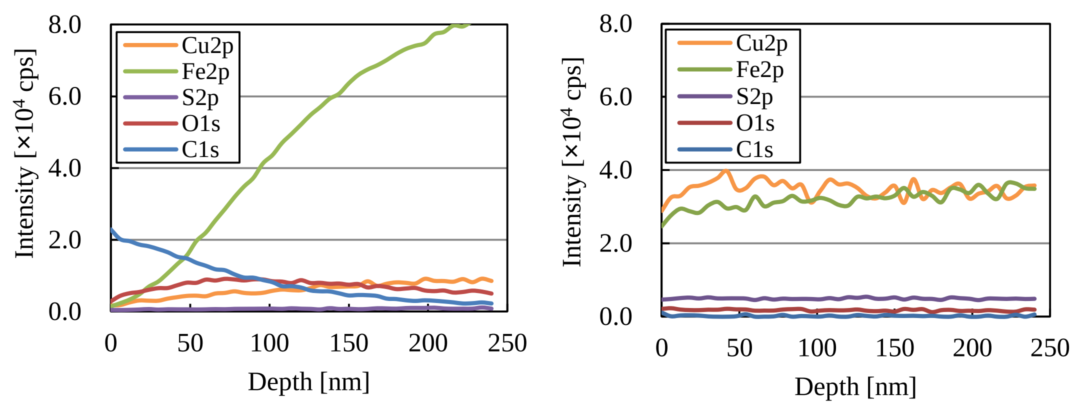


Figure 8: Wear amount and Vickers hardness.

As mentioned above, Cu_5FeS_4 is considered to be unsuitable as a solid lubricant at first glance because the friction coefficient is relatively high and the wear amount is large. However, when the shaft after the friction test was observed, a thin coating which could not be confirmed by other shafts could be visually confirmed on the surface of the S45C shaft which is a mating member of Cu_5FeS_4. From this fact, adhesion to the mating material was evaluated by performing elemental analysis in the depth direction by subjecting the mating shaft of the test specimen sintered only to Cu_5FeS_4 to X-ray Photoelectron Spectroscopy (XPS) analysis. The results of analysis in the depth direction by XPS analysis of the mating shaft of the specimen in which only Cu_5FeS_4 was sintered are shown in the Figure 9. From this figure, peaks of Fe2p and C1s, which are constituent elements of the shaft, are strongly observed in the non-sliding part (a) where the Cu_5Fe_4 is not in contact, and it is found that almost no S2p is detected. On the other hand, in the contact part (b), since S2p is observed in addition to Cu2p and Fe2p, it can be seen that the transfer film due to the sulfide is present and its thickness is 250 nm or more. Therefore, it can be said that Cu_5FeS_4 is a material satisfying the strong adhesion to the mating material, which is the performance required for the solid lubricant.



(a) Non sliding part (b) Sliding part (Cu_5FeS_4 transfer part)

Figure 9: Depth analysis result of shaft by XPS.

3.3.2 Sulfide dispersed bronze specimen

The average friction coefficients of the sulfide dispersed bronze test specimen are shown in Figure 10, the Vickers hardness of the test specimen and the surface roughness before and after the test are shown in Figure 11. The average friction coefficient is an average of the values of the friction coefficient from the test time of 60 seconds to 300 seconds. From Figure 10, it is understood that almost all the test specimens including the sulfide show lower friction coefficient than the bronze test piece not containing the sulfide, and the synthetic sulfide functions as a solid lubricant. Particularly, in the test piece to which 2 mass% of sulfide is added, there is a tendency to exhibit a low coefficient of friction, and the addition amount of sulfide is considered to be an appropriate amount around 2 mass%. Among them, the specimen to which Cu_2S or Cu_5FeS_4 is added shows a relatively low coefficient of friction of about 0.1 to 0.15 from the Figure 10 and it is understood that the friction characteristics are most improved. This is because the sulfide was uniformly dispersed on the friction surface and the Vickers hardness of the test piece containing

Cu_2S was smaller than the test piece containing other sulfide as shown in Figure 11. In the specimen containing Cu_5FeS_4, the roughness after the test is very small from Figure 11, so it is thought that Cu_5FeS_4 reformed the friction surface and the coefficient of friction greatly decreased due to the mild friction state. However, the test was carried out with the particle size of the sulfide uniformed to 63 μm or less, but since commercially available MoS_2 had an average particle size of about 3.5 μm and dispersion situation also fluctuated, it is thought that the particle size and area ratio of the sulfide may have influenced the result.

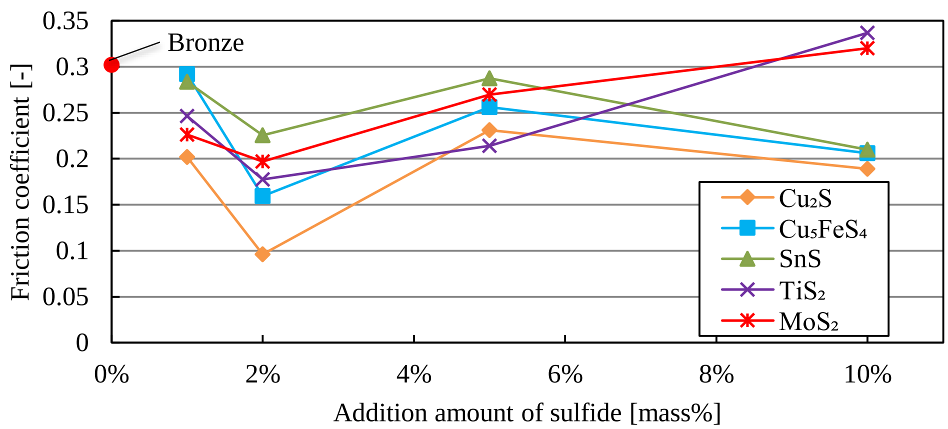


Figure 10: Average coefficient of friction (Sulfide dispersed bronze).

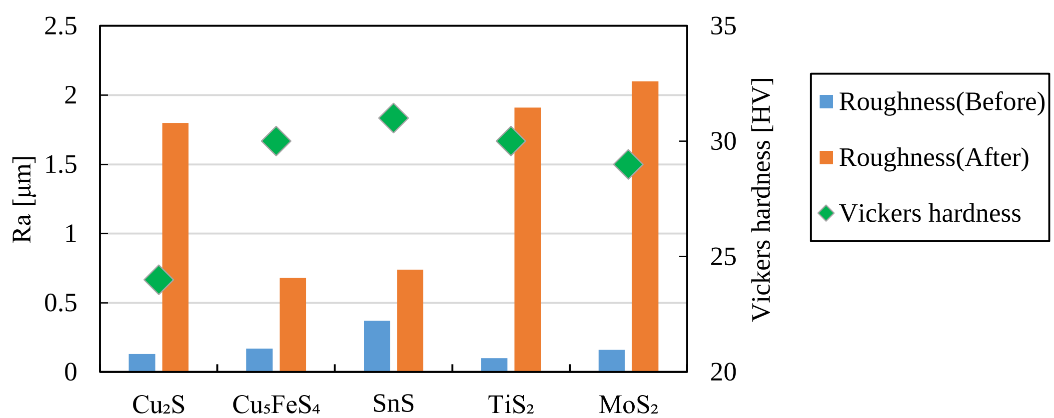
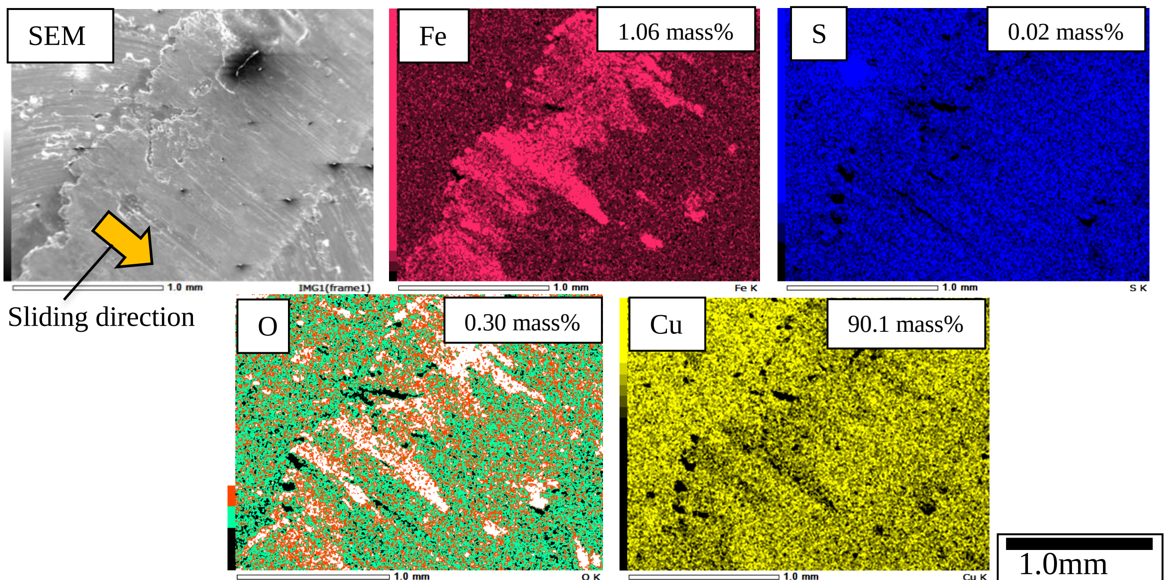
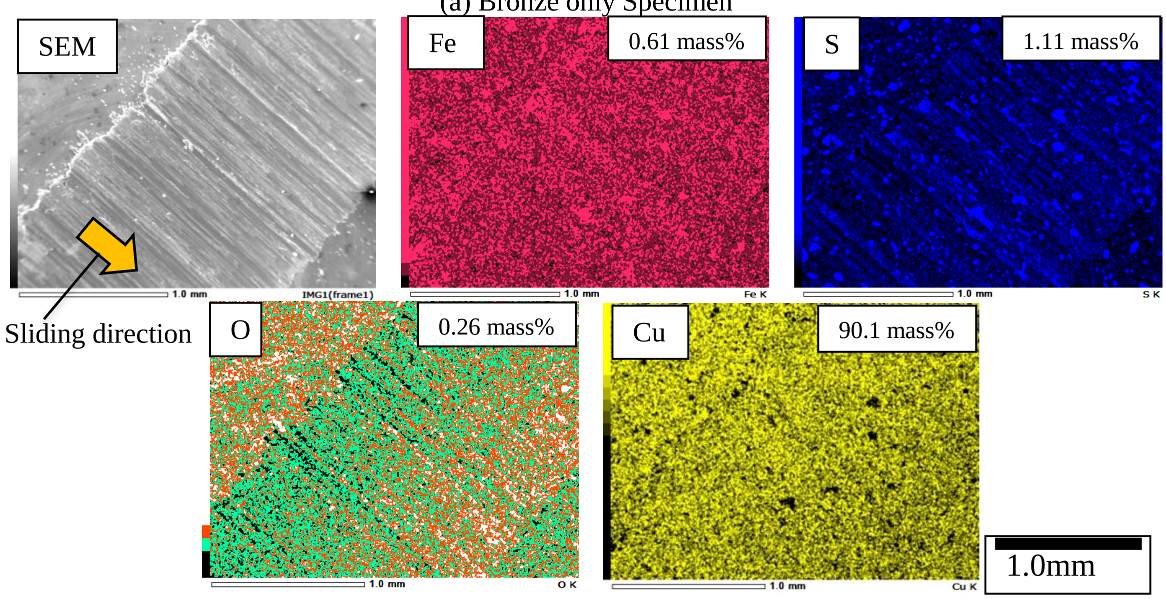


Figure 11: Surface roughness and Vickers hardness before and after the test (sulfide addition amount 2 mass%).

The scanning electron microscope and energy dispersive X-ray analysis (SEM / EDS) images of the sliding marks after the friction test of the test specimen with only bronze and the test specimen added with 2 mass% of Cu_5FeS_4 are shown in Figure 12. At the upper right of the EDS image, mass% of each element is displayed by simple quantitative analysis. From these results, it can be seen that the carbon steel as the mating material has widely adhered to the sliding mark of only bronze containing no sulfide. On the other hand, adhesion of carbon steel cannot be confirmed in the specimen containing sulfide, sulfide is uniformly present in the sliding mark from the element mapping of sulfur (S), and it can be seen that a thin film is formed. Due to the existence of this thin coating, the specimen containing Cu_5FeS_4 seems to have significantly decreased friction coefficient and surface roughness.



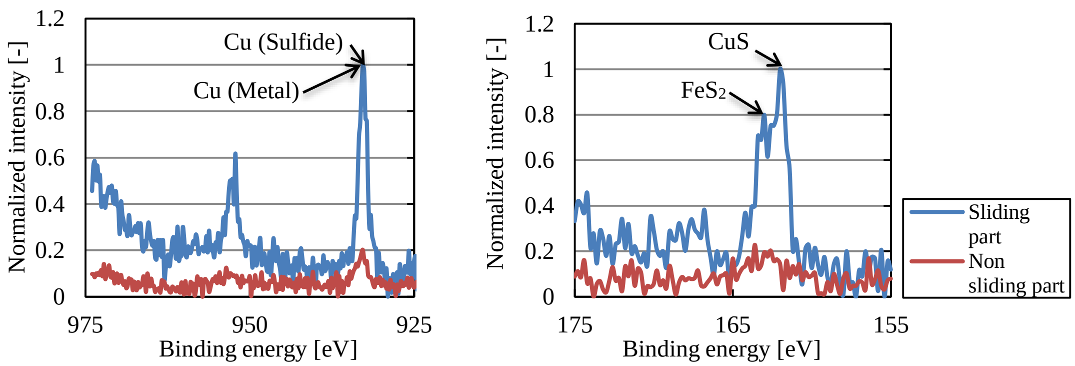
(a) Bronze only Specimen



(b) Sulfide-dispersed bronze test piece (Cu_5FeS_4 added at 2 mass%)

Figure 12: SEM / EDS image of specimen sliding mark.

Then, chemical state analysis of the shaft by XPS was carried out in order to confirm whether or not a sulfide derived coating was also formed on the shaft surface as the mating material. The XPS analysis results of the shaft of the test specimen containing Cu_5FeS_4 2 mass% are shown in Figure 13. From this result, it can be seen that not only Cu (metal) derived from bronze but also Cu (sulfide) and CuS and FeS_2 peaks are observed. From this, it can be seen that the sulfide also migrates to the mating material side, forming a thin tribo coating on the friction surfaces of both the test piece and the shaft. It is thought that this prevents direct contact between the base materials and achieves a low friction coefficient.



(a) Cu2p (b) S2p

Figure 13: Chemical state analysis result of shaft by XPS (Cu_5FeS_4 added 2 mass%).

4.0 CONCLUSION

It was found that various metal sulfides can be easily synthesized by a simple synthesis method in which metal powder and sulfur powder are mixed and vacuum heated. The merit of synthesizing from powders is that the crystal structure can be controlled by changing the heat treatment process and sulfides showing good sliding properties can be combined with each other.

It was found that the bronze test specimen containing the synthesized sulfide has a significantly lower friction coefficient and functions as a solid lubricant as compared with the bronze test specimen not containing the sulfide. Particularly, the test specimens containing Cu_2S and Cu_5FeS_4 at about 2 mass% exhibited a low coefficient of friction, which is not only due to the hardness but also from the results of SEM and XPS that a sulfide thin film was formed on the friction surface. This is similar to the mechanism of lead contained in lead bronze to reduce the coefficient of friction (Nojiri et al., 1971), and it can be said that non-toxic sulfide can replace lead.

ACKNOWLEDGEMENT

This research was financially supported by the Kansai University Grant-in-Aid for progress of research in graduate course, 2017.

REFERENCES

Directive 2011/65/EU of the Euroean Parliament and of the Council, 2011.

Hirai, Y., Sato, T. and Usami, H., 2016. Combined effects of graphite and sulfide on the tribological properties of bronze under dry conditions. Jurnal Tribologi, 11, 14-23.

Kato, K., Tagami, M., Yamada, S. and Takeda, T., 2002. Development of Solid Lubricants Dispersed Bronze Bearing Material by Powder Metallurgy (First Report). Journal of the Japan Society of Powder and Powder Metallurgy, 49(9), 812-817.

Kumar, P.S., Manisekar, K., Subramanian, E. and Narayanasamy, R., 2013. Dry sliding friction and wear characteristics of Cu-Sn alloy containing molybdenum disulfide. Tribology Transaction, 56, 857–866.

Nakayama, H., Nishio, T. and Kobayashi, K., 2010. Behavior of Bismuth in Solidification of Lead-free Bronze and Effects of Bismuth on Mechanical Properties of Casting. J.JFS, 82(2), 97-102.

Nojiri, T., Hayama, F. and Oya, S., 1971. Wear mechanism of lead-bronze on dry state sliding. J.Japan Inst.Met.Mater, 36(1), 39-45.

Sato, T., Hirai, Y., Fukui, T., Tanizawa, K. and Usami, H., 2012. Tribological properties of porous Cu based alloy containing nano sized sulfide particles. Journal of Advanced Mechanical Design, Systems and Manufacturing, 6(1), 158–167.

Tani, Y., 1982. Static Characteristics of the Load Cell Using for the Research of Cutting. Production research, 34(6), 211-218.

Tanizawa, K., Usami, H., Sato, T., Hirai, Y. and Fukui, T., 2012. Effects of penetrated graphite on tribological properties of copper based journal bearing. Key Engineering Materials, 523-524, 805-808.

Wada, H., Takeda, K. and Sasaki, T., 2004. DSC studies on reactions of the elements with sulfur. State Ionics, 172, 421-424.