Synthesis and Functional Evaluation of Sulfides : Application of Solid Lubricant and Thermoelectric Material

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Synthesis and Functional Evaluation of Sulfides: Application of Solid Lubricant and Thermoelectric Material

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Abstract

Sufides as MoS_2 are known as solid lubricants. These materials are also known as thermoelectric materials. However, there is no material satisfying both functions at the same time. In this study, sulfides powders such as Cu_2S (chalcocite), TiS_2, SnS, Cu_5FeS_4 (bornite) were synthesized under vacuum condition. Some specimens of sintered sulfides were evaluated by friction tester and their lubricity. As a result it was found that SnS had indicated better friction properties. Other specimens were evaluated in terms of Seebeck coefficients, which is one of the thermoelectric properties. Experimental results of the Seebeck coefficients were compared with simulation results. For thermoelectric properties, the Seebeck coefficient of Cu_2S had matched with experiments and simulation. Totally, Cu_2S (chalcocite) and SnS has superior properties both, as solid lubricant as well as thermoelectric material.

1. Introduction

Thermoelectric materials are focused in so called energy harvesting research field. By using waste heat, it turns on electric power through the thermoelectric materials. Generally, oxide system as TiO_2, non-oxide system as Bi-Te system are popular thermoelectric materials. One of the candidates of non-oxide system are sulfide materials. For example, CZTS (Cu_2ZnSnS_4) is a well-known material not only for solar cells but also for thermoelectric materials. These thermoelectric materials are semiconductors. Cu-S systems like Cu_2S (chalcocite) which is a thermoelectric sulfide is a positive semiconductor, and it turns into a negative semiconductor by adding Fe as $CuFeS_2$.

On the other hand, sulfides are also well known as solid lubricants. MoS_2 and WS_2 are well known sulfides and their unique micro structure which is layered structures is the reason why they slide well on the friction surfaces. Moreover, the micro structure is also key of high performance as thermoelectric materials. However, it is not reported that both functions thermoelectric and solid lubricant are exhibited at the same time. If both functions will exhibit at the same time, applications as below will be proposed.

The feature of ordinary thermoelectric elements is that it can produce electric power not preparing driving or rotating parts as a generator. It seems that electric power is also produced if a thermoelectric element or device has a driving or rotating part by closing to each other. It means that heat flow by friction between thermoelectric element and driving or rotating part make enables production of electric power. If not enough electric power is produced, it has the possibility to be used as a sensor. The sensor named “tribocensor” will be able to satisfy the needs of tribotronic fields [1].

In this study, sulfides are synthesized which shall exhibit both functions, thermoelectric and solid lubricant, at the same time. Cu_2S and, Cu_5FeS_4 (so called bornite) which are already known for their good behavior as solid lubricants [2], dispersed in bronze, SnS and TiS_2 were the investigated materials in this study. At first, thermoelectric properties are evaluated by comparing experimental results and simulation results that are based on first principle simulation conducted for several sulfides. In this comparison, the Seebeck coefficient, which is one of the important properties of thermoelectric abilitie, is evaluated. Beside the friction properties of synthesized sulfides manufactured by sintering process are also evaluated.

Different synthesizing processes for sulfides, especially, vacuum sintering method is adopted in this study. Not only the production of sulfides but also sulfide dispersed bronze were sintered in vacuum atmospheres.

2. Theory

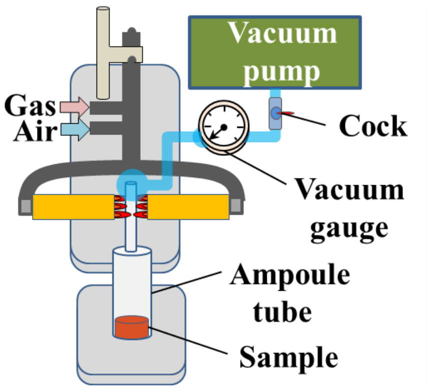


Fig.1 Vacuum enclosing device

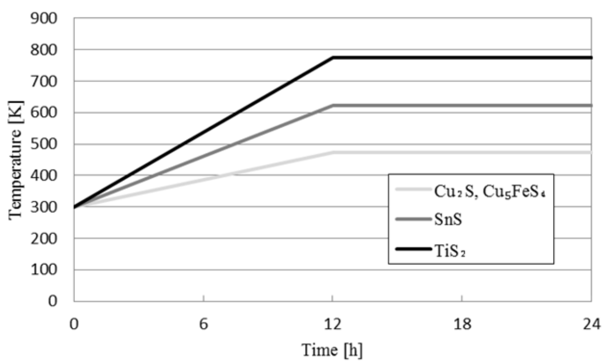


Fig.2 Synthesis temperature and time

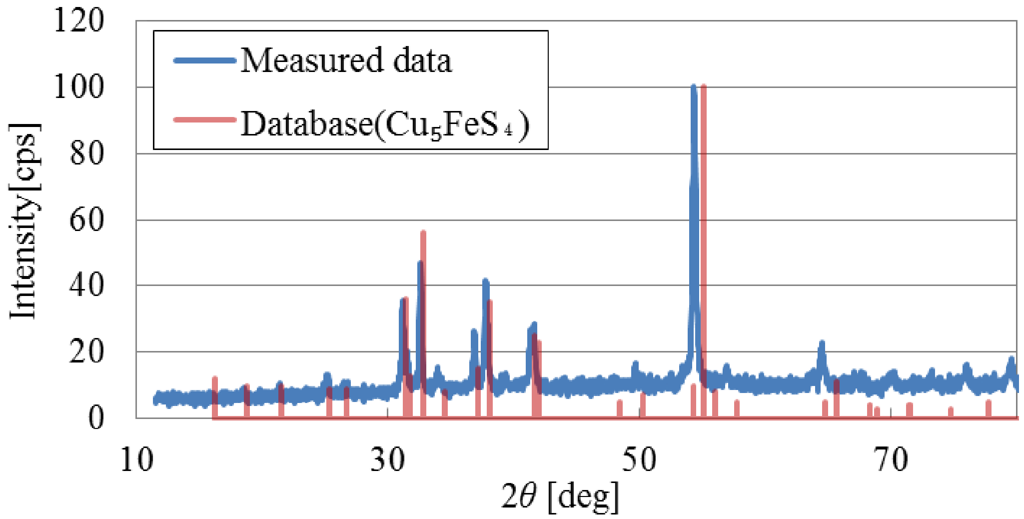


Fig.3 X-ray diffraction results of Cu_5FeS_4

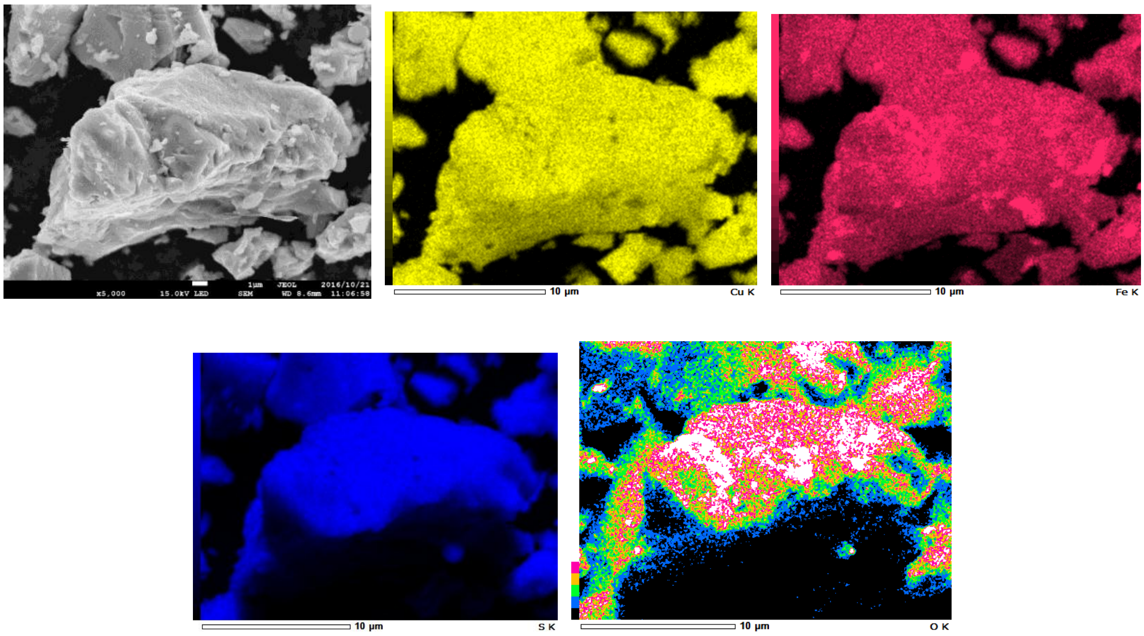


Fig.4 EDS results of synthesized Cu_5FeS_4 (bornite)

2.1 Preparation of sulfides

For synthesis of sulfides, powders for each element, namely sulfur (S), copper (Cu), iron (Fe), tin (Sn) and titanium (Ti) were prepared. After mixing these powders in the right stoichiometry, the powders were enclosed in ampoules shown in Fig.1 at about 0.67Pa. The temperature profile for the synthesis of each sulfide is shown in Fig.2. These graphs were determined by literature data. For synthesis of pure thermoelectric materials, the vacuum atmosphere, had a pressure of 0.67Pa, which is a moderate vacuum value for engineering sulfide powders like solid lubricant as Cu_2S, even though many thermoelectric materials need to synthesize at very high vacuum atmosphere. The reason why sulfides were synthesized at moderate vacuum atmosphere was to make manufacturing in industrial equipment easier possible. Fig.3 shows the results of X-ray diffraction (XRD) of Cu_5FeS_4 (bornite). The main peaks almost matched the data known from the database. Not only Cu_5FeS_4 but also Cu_2S, SnS, TiS_2 were confirmed as well synthesized sulfides by the results of XRD. Fig.4 shows the results of EDS (Energy dispersive X-ray spectrometry). A particle in the figure indicated Cu, Fe and S. From results of XRD and EDS, it was confirmed that sulfides were well synthesized. However, oxygen was also observed on the particles in Fig.4. It seems that some oxides existed on the sulfides. After synthesis of the sulfide powders, sulfides were compacted as green bodies and sintered in vacuum atmosphere. Fig.5 shows the temperature profile of sintering of the sulfides (Cu_2S, Cu_5FeS_4 and SnS). Here, TiS_2 was not sintered in these conditions because it is likely to react with the low amount of oxygen in the vacuum atmosphere.

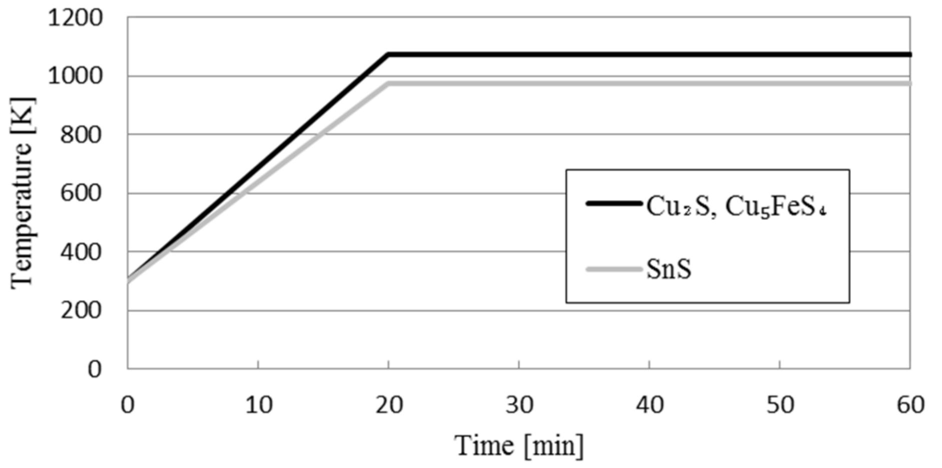


Fig.5 Sintering temperature and time

2.2 Simulation conditions

When the Seebeck coefficient of the experimental data was compared with simulation data, firstly, first principle calculation was conducted to clarify energy, density of states and band structures of every sulfide unit cell. In this study, WIEN2k which is a software package for first principle calculation was used. By setting, elements and structural data as input data, calculation could be done.

After the calculation, BoltzTrap which is software package for transport coefficients calculation based of Boltzman equations was used. At that time, energy and structure data of system calculated by WIEN2k was inputted as initial conditions for BoltzTrap.

In table 1, crystal data of sulfides by using WIEN2k calculation are indicated.

Table 1 Crystal data

	TiS_2	Cu_2S	Cu_5FeS_4
a,b,c[Å]	3.405, 3.405, 5.695	3.89, 3.89, 6.88	10.8785
α,β,γ[deg.]	90, 90, 120	90, 90, 120	90
Number of atoms	3	3	6
Space group	164_P-3m1	173_P63	216_F-43m

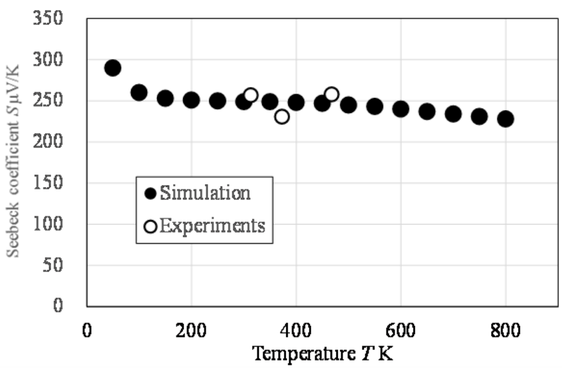
2.3 Friction test

Friction test was conducted by using journal type apparatus to realize line contact conditions between specimen which were mirror polished sulfide in this study and mating materials which is a machine finished steel shaft called S45C restricted in Japan Industrial Standard (JIS). Details of test conditions are indicated in table 2.

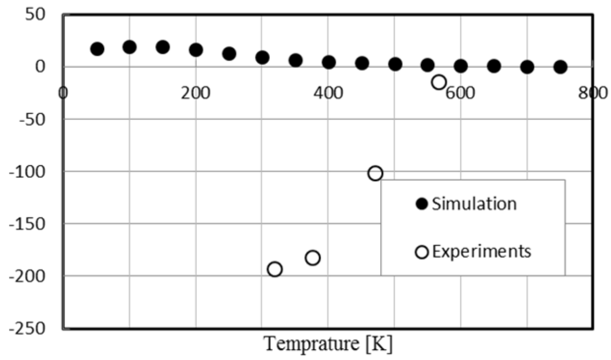
A friction test was done under dry condition at room temperature. The test was stopped as soon as seizure occurred.

Table 2 Friction test conditions

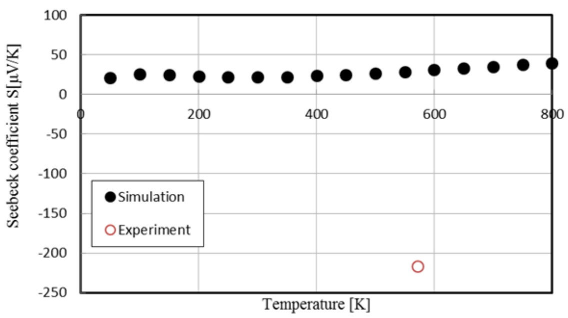
Environment	Dry
Test temperature	RT
Load	7.35 N
Test time	300 sec
Rotation speed	3.14 m/sec(10000 rpm)
Material of the shaft	S45C (No heat treatment)

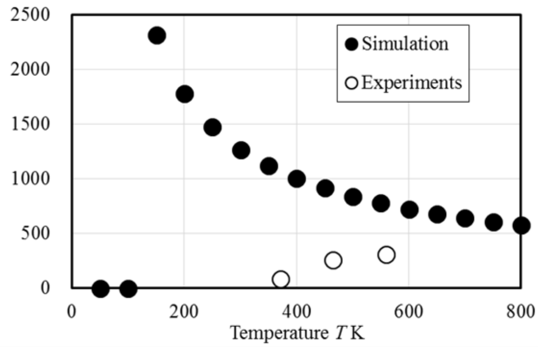


(a) Cu_2S



(b) Cu_5FeS_4





3.Results and discussions

3.1 Seebeck coefficient

Figure 6 shows the Seebeck coefficient for Cu_2S, Cu_5FeS_4, TiS_2 and SnS. Experimental data of the Seebeck coefficient were observed at room temperature, 373K, 473K and 573K. On the other hand, simulation data was plotted from 50K to 800K, every 50K. From the result, experimental data and simulation data of Cu_2S matched well around room temperature to 473K. On the other hand, the simulation results of Cu_5FeS_4, TiS_2 and SnS did not match the experimental data. Cu_5FeS_4 (bornite) had a negative Seebeck coefficient which was equal to negative semiconductor even other experimental data and literature shows it was positive [3]. However, simulation results changes positive to negative. Results of TiS_2 also shows opposite data between experimental and simulation. By adding other elements, some sulfides change positive/negative to negative/positive semiconductor, impurity material could contain in the synthesis sulfide. It might be difficult for XRD to detect impurity because the present amount might have been too low. Here, impurity means that artificial bornite, Cu_5FeS_x (X=2, 3 or 4) in Cu_5FeS_4 or TiO_2 in TiS_2. SnS had positive coefficient and shows better value among the synthesis sulfide in this study.

3.2 Friction properties

Described as 2.3 and Table2, Fig.7 shows the results of friction test and Fig.8 shows wear amount during the test and Vickers hardness of specimens before the test. Cu_2S showed the highest coefficient of friction. The friction test for Cu_2S was stopped after 130 sec. due to the fact, that wear was very severe (shown in Fig.8). On the other hand, Cu_5FeS_4 and SnS had finished the test without seizure and significant wear. From these result, Cu_5FeS_4 and SnS had better friction and wear properties. Especially, SnS showed the lowest coefficient of friction and lowest wear mount among the three sulfides.

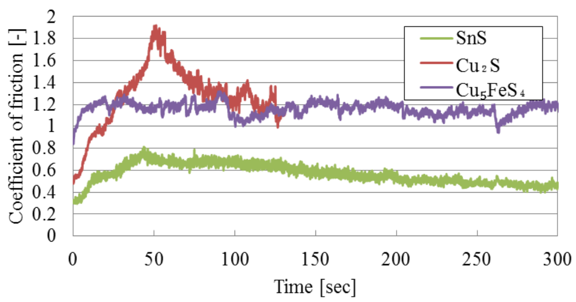


Fig.7 Results of friction test

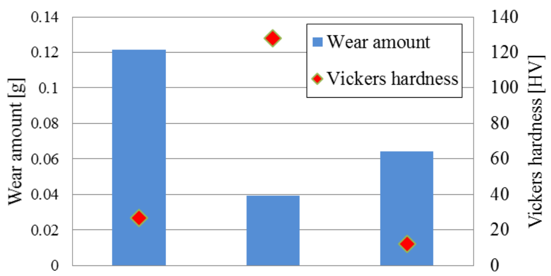


Fig.8 Wear amount and Vickers hardness

4. Summary

Sulfides which have been synthesized in vacuum atmosphere can be used as thermoelectric material as well as solid lubricant. For thermoelectric properties, Seebeck coefficient of Cu_2S showed a good match between experimental and simulation results. It might be that Sn-S system is providing superior properties for functions as thermoelectric material as well as solid lubricant. Cu_2S (chalcocite) and SnS has superior properties as both solid lubricant and thermoelectric material.

Acknowledgement

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