Effect of Calcium Compounds in Lubrication Oil on the Frictional Properties of Fe_2O_3 – Al_2O_3 Ceramics under Boundary Lubricating Conditions

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酸化鉄–アルミナ複合セラミックスの境界潤滑域での摺動特性に及ぼす潤滑油中のカルシウム化合物の影響

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Calcium sulfonate, a detergent/dispersant component in lubricating oils, greatly increase the friction coefficient of TiO_2 added Fe_2O_3 – Al_2O_3 ceramics under boundary lubricating conditions. ESCA studies showed that the average thickness of an organic thin film sticking to the surface of wear tracks was thicker than that away from wear tracks, and the concentrations of Ca, S and P were much higher in the wear track than those off the wear track, suggesting that most of the $-\text{SO}_3$ –Ca–OH groups in sulfonate remained unchanged. It is concluded that oil containing rich calcium compounds possibly formed a layer, blocking other oily additives with which the surface would have been wettable. This is assumed to increase the friction coefficient of the TiO_2 added Fe_2O_3 – Al_2O_3 ceramics.

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1. Introduction

Ceramics, which are lightweight and have excellent wear resistance, are promising materials for sliding parts, such as bearings and engine components. Many sliding parts are used with lubricating oil, and the frictional behavior of systems incorporating such parts varies depending on the contact state between solids affected by the oil viscosity and the interaction between the lubricant ingredients and solid ceramic surface. Commercially available lubricating oils are mostly designed and synthesized specifically for metal surfaces: such lubricants may not be applicable to ceramic surfaces. It is expected that novel lubricating oils will be developed to effectively exploit the advantages of ceramics in the future.

Despite the numerous studies on solid-solid or solid-simple lubricant (e.g., water) interactions,^{1)–5)} few detailed studies have addressed sliding phenomena and the influence of specific ingredients in lubricating oils for ceramics.

Gates and Hsu reported the effect of various kinds of sulfonates and phosphates in oil on the frictional properties of hot pressed silicon nitride ceramics.⁶⁾ They found that the friction coefficient varied greatly according to the types of the additives in paraffin oil.

The present authors have reported the influence of the addition of detergent/dispersant on the friction coefficient of Fe-compound dispersed ceramics.^{7),8)} However, details of the chemical state of the organic matter in the wear tracks remain unclear. Thus, the present study was aimed at elucidating the effects of the detergent/dispersant ingredients calcium sulfonate and calcium carbonate on the frictional properties of lubrication oil and the chemical states and compositions of oil films forming in the wear tracks of Fe_2O_3 – Al_2O_3 composite ceramics.

2. Experimental

2.1 Specimen preparation and properties

The raw materials used in this study include Al_2O_3 (A-32, Nippon Light Metal Co., Ltd.), Fe_3O_4 (MAT-305, Toda Kogyo Corp.) and TiO_2 (TIO06PB, Kojundo Chemical Lab. Co., Ltd.). Al_2O_3 , Fe_3O_4 , and TiO_2 were mixed in the ratio 65 : 30 : 5 (mass%). A 3 mass% PVB (polyvinylbutyral) binder and ethanol were added. The mixture was ball-milled for about 24 h and then spray-dried. The resultant powder was uniaxially pressed and then molded by CIP (cold isostatic press) at about 400 MPa. The green body obtained was sintered at a maximum temperature of 1773 K for 3 h in an air furnace. This sintered product is hereinafter referred to as the “FAO composite ceramic”.

In our previous report,⁷⁾ SiO_2 added Fe_2O_3 – Al_2O_3 composite ceramics was used as test specimens. In the present study, TiO_2 added Fe_2O_3 – Al_2O_3 was used because it was found that the addition of TiO_2 improved strength.

The microstructure of the FAO composite ceramic is shown in Fig. 1. Energy dispersive X-ray spectroscopy (EDS) confirmed that the dark and bright portions in the micrograph were rich in Al and Fe, respectively. XRD analysis revealed the presence of Al_2O_3 , Fe_2O_3 and AlFeO_3 . The Fe_3O_4 , used as raw material, transformed into Fe_2O_3 after sintering. The FAO composite ceramic exhibited an average four-point bending strength of 322 MPa and a Vickers hardness of around 11 GPa.

2.2 Evaluation of frictional properties

2.2.1 Instrument description and testing conditions

A back and forth motion type friction tester (Kyowa Giken Co., Ltd.) was used. A plate and pin were used as specimens for friction testing. A movable plate was in contact with the

Fig. 1. SEM image of TiO₂ added Fe₃O₄-Al₂O₃ ceramics.**Table 1.** Values of Viscosity, and Chemical Composition of Additives in SAE10W-30 Lubricant

Viscosity/mm ² ·S ⁻¹		Chemical Composition/mass%					
at 313K	at 373K	N	Ca	Zn	S	B	P
67.4	10.2	0.04	0.45	0.12	0.58	0.04	0.11

lower test surface of a fixed pin and moved in horizontal reciprocating motion. Sliding was performed at a velocity of 0.524 m/s, a temperature of 373 K, under a load of 88.2 N. It was confirmed that these conditions represented boundary-lubricating conditions.

2.2.2 Description of specimens

The plate specimen was made from the above-mentioned FAO composite ceramic. It was rectangular, 10 mm in thickness, 15 mm in width, and 65 mm length, with a sliding-surface roughness $R_{\max}$ of 0.8 μm or less. The pin used was made from Cr-plated cast iron, which is widely used in piston rings because of its high performance as a sliding material. The specimen geometry was φ8 mm, 23 mm long, with a tip radius of SR18, and an $R_{\max}$ identical to that of the plate.

2.2.3 Lubricating oil

SAE10W-30 was used, a general-purpose lubricating oil for engines, composed mainly of mineral oil. Generally, the relationship between the temperature and viscosity of a lubricating oil is expressed by the Walther equation.⁹⁾

$$\log \log (\nu + 0.7) = m \log T + b \quad (1)$$

where ν is the kinematic viscosity, m and b are oil-specific constants, and T denotes the absolute temperature. **Table 1** lists the viscosity of the lubricating oil SAE10W-30 and the chemical composition of additives. SAE10W-30 typically also contains various additive agents, such as detergent/dispersant, an oxidation inhibitor, extreme pressure agents, and oily additives containing Ca, P, S, and Zn. The detergent/dispersants are lime compounds, namely calcium sulfonate and calcium carbonate. Alkyldithiophosphoric acid is used as an oxidation inhibitor. **Figure 2** shows the constitutional formula of the additives that are often contained in the oil.¹⁰⁾ The specifications for the oil used in this test were not provided by the manufacturer, thus we tried to determine them using ESCA.

2.2.4 Oil preparation with different composition

To investigate the influence of the mixing ratio on the friction coefficient, friction tests were conducted using two types

(A) Calcium sulfonate

(B) Alkyldithiophosphoric acid

Fig. 2. Constitutional formula of additives in the test oil.

of lubricating oils (type A and B). The lubricants were prepared as follows.

Type A: The detergent/dispersant was added to the base oil (mineral oil) in different proportions. The mixing ratio of calcium sulfonate to calcium carbonate in the detergent/dispersant was fixed to 89:11 by mass, which is equivalent to the ratio in the commercially available SAE10W-30.

Type B: Lubricants with 7 mass% (fixed) calcium sulfonate and various amounts of calcium carbonate were prepared. In SAE10W-30 oil, the content of calcium sulfonate was found to be approximately 7 mass%.

2.3 Analytical procedures

Electron spectroscopy for chemical analysis (ESCA) was used to analyze surfaces in and off the wear track after friction experiments in terms of the chemical structure of calcium-containing polymers. The oil adhering to the sliding surface was wiped lightly with a paper towel, and subjected to the analysis described below. The specifications of the instrument used and the measurement conditions were as follows.

- **Instrument** : photoelectron spectrometer (SSX-100/206; Surface Science Instruments)
- **X-rays** : Monochromatized Al-K alpha 1 and 2 (1486.6 eV)
- **X-ray beam shape** : Ellipse (a : 600.150 μm, b : 1.74 × a)
- **Photoelectron escape angle (theta)** : 35°
- **Energy adjustment** : the bonding energy of Cl's main peak at 284.6 eV

3. Results and discussion

3.1 Effect of detergent/dispersant on frictional properties

Figure 3 shows the friction coefficients obtained under boundary lubricating conditions using lubrication oils with various concentrations of detergent/dispersant. **Figure 3** indicates that the friction coefficient of the FAO composite ceramic gradually increases with the addition of detergent/dispersant.

Figure 4 shows the relationship between the calcium carbonate concentration and the friction coefficient. In this test, the calcium sulfonate content was fixed at 7 mass%, which is equivalent to that of commercially available SAE10W-30. As shown in **Fig. 4**, the friction coefficient does not increase with further addition of carbonate.

As can be seen in **Fig. 4**, the lubricant with 7 mass% calcium sulfonate and 0.1 mass% calcium carbonate added oil (data B) increased the friction coefficient greatly (data B)

Fig. 3. Friction coefficients under boundary lubricating conditions according to the amount of detergent and dispersant addition.

Fig. 4. Relationship between calcium carbonate concentration and the friction coefficient under boundary lubricating condition.

compared to the case of using the base oil (data A), namely from 0.0365 to 0.082.

The ratio of the increases in friction coefficient per unit mass of calcium sulfonate addition was estimated to be $(0.082-0.035)/7=0.0067$. Here, the addition of calcium carbonate was negligible. By contrast, 7 mass% calcium sulfonate and 2 mass% calcium carbonate added oil yields a μ of 0.096 (data C). Thus, the ratio of the increases in friction coefficient per unit mass of calcium carbonate addition was estimated to be $(0.096-0.082)/1.9=0.0073$. That is, it can be said that the effects of calcium sulfonate and calcium carbonate were almost same or the latter had larger effects. As mentioned above, the detergent/dispersant is composed mainly of calcium sulfonate, thus the increase of the friction coefficient by the addition of detergent/dispersant (see Fig. 3), was controlled by calcium sulfonate.

3.2 ESCA analysis of oil films in the wear tracks

3.2.1 Quantitative analysis

Chemical analysis of oil films was carried out, mainly with regard to the detergent/dispersant discussed above as the cause for the increase in the friction coefficient, to elucidate their condition on the surface. Sliding tests were performed using the standard lubricant SAE10W-30. Then, the specimen surface was wiped lightly with a paper towel and analyzed.

Elements on and off the wear tracks after a sliding experiment were detected using a wide scan, as shown in Fig. 5. The results are classified, quantified (at%, atomic ratio) and summarized in Fig. 6. Detected elements include C, Ca, Zn, S, Sn and P in oil, as well as constituents of ceramics, such as Al,

Fig. 5. Detected elements in and off the wear tracks after a slide experiment.

Fig. 6. Summary of atomic ratio for each elements.

Fe, Ti and O. The extra elements are presumed to be from an organic thin film on the ceramic surface. As shown in Fig. 6, the concentrations of Ca, P and S are much higher in the wear track than off the wear track. The lower concentration of Al,

Table 2. Peak Positions of Major Elements Detected from in and off the Wear Tracks

	Al2p	Fe2p _{3/2}	Ti2p _{3/2}	O1s	Ca2p _{3/2}	Zn2p _{3/2}	S2p	Sn3d _{5/2}	P2p
Off wear track	73.9	711.2	457.8	530.8	347.3	1021.5	168.4	486.4	-
On wear track	73.7	710.6	-	531.1	347	1021.6	167	-	133.1

Fig. 7. Separation of peaks belong to carbon (C1 peak).

Fig. 8. Analysis of separated peaks belong to carbon (C1 peak).

Fe, and Ti on as compared to off the wear tracks suggests that the average thickness of the organic thin film sticking to the surface is relatively large: the film is presumably formed by sliding between the solids.

3.2.2 Analysis of peak positions

The peak positions of the main elements detected in and off the wear tracks are shown in Table 2. The peaks due to carbon (C1 peak) are then separated, as shown in Fig. 7, and the results are summarized in Fig. 8. Many compounds that are assignable to carbon are possible. CO_3^{2-} ions are observed in the wear tracks, while off the wear tracks, these are below the detection limit. Wear tracks show a slightly higher concentra-

Fig. 9. Schematic diagram of chemical state around wear track.

tion of the $-\text{COO}-$ group than regions off the wear tracks. The analyses for the other elements were conducted in a similar fashion.

On the basis of these results, the chemical state of the various elements can be described as follows: (a) Sulfate: Compounds that belong to $-\text{SO}_2-$ or SO_3- and carbon components assignable to $>\text{C}-\text{S}-$ or S are detected in the wear tracks. Although a small amount of S is detected off the wear tracks, it is thought that the same components are present off the tracks as on them. No inelastic-scattering peaks derived from bonds with the substrate materials were detected. (b) Phosphor: The peak position suggests that the phosphor detected on the wear tracks is attributable to phosphoric acid. (c) Calcium: On the wear tracks, the Ca concentration is much higher than the S concentration, as shown in Fig. 6. This cannot be explained by the presence of $-\text{SO}_3-\text{Ca}-\text{OH}$ bonds, as shown in Fig. 2. The presence of CO_3^{2-} and phosphoric acid implies that Ca is present as calcium carbonate or calcium phosphate in the wear tracks. Away from the wear tracks, the concentration of CO_3^{2-} is below the detection limit and the concentrations of Ca and S are almost the same. This means that most of the $-\text{SO}_3-\text{Ca}-\text{OH}$ groups remain unchanged, suggesting that Ca occurs not deep in the substrate material, but rather, adheres to the surface because no inelastic-scattering peak due to $\text{Ca}2\text{p}$, a component of detergent/dispersant, is observed in the wear tracks. (d) Zinc: the peak positions indicate that the Zn occurs as Zn^{2+} , both on and off the wear tracks. No inelastic-scattering peak from bonds with the substrate material is detected. On the basis of the analysis results, Figure 9 schematizes the chemical state of the additives in oil.

The detergent/dispersant used in this study contain calcium sulfonate and calcium carbonate, which presumably neutralize acids and disperse insoluble substances such as sludge. Calcium carbonate neutralizes acids and forms different salts in lubricating oils, e.g., in the case of H_2SO_4 : $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$. It is unlikely that H_2SO_4 is formed in the present experiments. Nevertheless, the ESCA results show that calcium carbonate and calcium sulfonate most likely stick onto the sliding surface of the FAO composite ceramic physically, rather than via chemical reactions. Detergent/dispersant possibly formed a thick layer, blocking extreme pressure materials or oily additives that would have been active. This is assumed to increase the friction coefficient of the FAO composite ceramic.

4. Conclusion

The present analytical study revealed the frictional properties of TiO₂ added Fe₂O₃-Al₂O₃ composite ceramics and oil films generated in the wear tracks:

(1) The detergent/dispersant components calcium sulfonate and calcium carbonate increase the friction coefficient markedly, even in trace amounts.

(2) ESCA study showed that the average thickness of an organic thin film sticking to the surface of wear tracks was thicker than away from the wear tracks, and the concentrations of Ca, S and P are much higher in the wear tracks than off the wear tracks, suggesting that most of the -SO₃-Ca-OH groups in sulfonate remain unchanged.

(3) It is presumed that oil-containing rich calcium compounds possibly formed a layer, blocking other oily additives with which the surface would have been wettable. This is believed to increase the friction coefficient of the TiO₂ added Fe₂O₃-Al₂O₃ ceramic.

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