Changes in Microstructure and Properties of ZnO-Added Al₂O₃ upon Sliding

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The changes in microstructure and properties of ZnO-added alumina upon sliding under water lubrication were studied. Although the frictional force was lower than that of conventional alumina in the early stages, it increased upon long-term friction testing. Of the acicular ZnO-nAl₂O₃ (n=3-9) and granular ZnAl₂O₄ phases dispersed in the samples, ZnAl₂O₄ with its low hardness was worn preferentially and pulled out during testing. The increase of frictional force during the sliding process was attributed to the pull-out of ZnAl₂O₄ particles and their traction on the sliding surface during the experiment.

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1. Introduction

Alumina is the most commonly used ceramic materials for mechanical seals. Silicon carbide and diamond-like carbon (DLC) have excellent friction properties. However, their high cost and the difficulty in scaled-up production remain as obstacles to the use of these materials, despite their highly superior underwater frictional properties compared to those of alumina. Thus, the present authors have attempted to develop alumina-based materials with more suitable properties for mechanical seals. More specifically, the present study addresses the development of an alumina material with excellent hydrophilic properties, wherein a water film is held between sliding surfaces without grease. The water film acts as a lubricant to relieve direct contact between the two solids, thereby reducing friction and wear. Enhanced lipophilic properties and a reduced frictional coefficient in the fluid and mixed-lubrication regions are reported along with iron compound particles and silicon nitride. However, adopting water, with its lower viscosity than that of oil, as a lubricant requires further enhancement of the hydrophilic properties of ceramics. Studies involving oxide systems include the enhancement of hydrophilic properties and water repellency because of the Si–H bonds on the surface of amorphous silica, and the formation of hydrophilic surfaces using the photocatalytic effect of titanium oxide. However, few studies have addressed oxide ceramics, fewer still alumina ceramics. To the best of our knowledge, none have examined wettability with water to improve frictional properties under water lubrication. Through a series of studies on alumina-based materials with enhanced hydrophilic properties, the present authors have identified that ZnO is as an effective additive for improving the hydrophilic properties of alumina, although the mechanism remains unclear. The present study is intended to analyze the changes in the microstructure and properties of this material that occur mainly upon long-term sliding.

2. Experimental procedures

2.1 Sample preparation

The raw materials employed in this study included Al₂O₃ (A-32; Nippon Light Metal Co., Ltd.), ZnO (ZN002PA; Kojundo Chemical Laboratory Co., Ltd.), and TiO₂ (A-100; Ishihara Sangyo Kaisha, Ltd.); the composition of specimens was 89:10:1 by weight, respectively. The powder was mixed with 5 mass% binder and 140 mass% distilled water for at least 12 h in a ball mill, then granulated using a small spray-dryer (LT-8; Ohkawara Kakohki Co., Ltd.), and classified with a 100-μm aperture sieve. The resultant powder was filled into a die and preformed with an uniaxial press under 39.2 MPa, then subjected to CIP at 343 MPa. Finally, the specimens were sintered at 1550°C for 3 h in air.

2.2 Evaluation method

2.2.1 Microstructure

Densities of the samples obtained were measured using Archimedes’ method. The phases were identified by microstructural observation of the sample surface by scanning electron microscopy (SEM; JSM-820; JEOL) and X-ray diffractometry (XRD; Mac Science Ltd.).

2.2.2 Hydrophilic properties

The contact angle of each sample was measured to determine its water-wettability. First, the sample surface was lapped and ultrasonicated for 15 min in acetone. Then, a micropipette was used to deposit a 0.5 ml drop of tap water onto the sample surface after drying. The contact angle was measured using an exclusive measuring apparatus (360 S-VHT; Elma).

2.2.3 Surface analysis using XPS

X-ray photoelectron spectroscopy (XPS) was used for characterization of specimen surfaces before and after sliding tests in tap water. XPS spectra were obtained by using an SSX-100/206 (Surface Science Instruments), operating at a pressure of approximately 1.33 × 10⁻⁷ Pa and unmonochromated Al Kα radiation. X-ray beam size was 600 μm. The binding energy was referenced to the C1s spectra of an adven-
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Fig. 1. Frictional coefficient of the 10 mass% ZnO-added alumina and normal alumina with test cycles.

Fig. 2. Comparison of frictional coefficient between initial and last stage for alumina with different ZnO content.

Frictional properties were evaluated using a reciprocating-motion type friction tester. This testing machine contacts a movable plate (area: 314 mm²) completely to the lower test surface of a fixed circular disc, then operates the plate so that the two objects undergo horizontal reciprocating motion. Here, the same material was used for the plate and disk. Sliding was performed at a velocity of 0.002–0.0083 mm/min, under a load of 210 N, with tap water dripped continuously on the sliding surface. Tests on conventional ZnO-free alumina under these conditions proved that boundary-lubrication was achieved.

3. Results and discussion

Figure 1 plots the frictional coefficient of conventional (ZnO-free) and 10 mass% ZnO-added alumina as a function of the number of sliding cycles. As shown in Fig. 1, ZnO-added alumina shows a frictional coefficient of 0.4 in the early stages, gradually dropping to 0.2 at 5500 cycles. By contrast, conventional alumina shows a high frictional coefficient of 0.6–0.8 in an early stage (<500 cycles).

Figure 2 compares the frictional coefficient of samples of varying ZnO content in the initial (around 200th cycle) and final stages (around 10000th cycle) of sliding tests. As shown in Fig. 2, for samples with low ZnO content, the frictional coefficient in the initial stage is equivalent to that in the final stage. The difference in frictional coefficient between the initial and final stages increases according to the content of ZnO.

It is believed that the friction coefficient under boundary lubrication conditions is strongly affected by the water-wettability of the surface. Thus, the change in wettability was evaluated.

Figure 3 shows the measured water contact angle of the 10 mass% ZnO-added alumina sample before and after the sliding test ~40° and ~70°, respectively. This result suggests that after the sliding test, the surface becomes less wettable to water.

It is well known that wettability of a surface is controlled by the chemical and physical factors, such as change in polarity due to chemical reactions and change in surface morphology. Several studies were conducted to investigate these factors.

Figure 4 shows ESCA analysis profiles of the 10 mass% ZnO-added alumina sample before and after endurance testing. Of the elements contained in tap water, Ca, Mg, and Cl showed few change throughout the test. Thus, it seems that the present ESCA analysis reveals the absence of any chemical reaction between impurities in tap water and the test piece surface that degrade frictional properties.

Figure 5 presents SEM images of the 10 mass% ZnO-added alumina samples before and after the sliding test. Before the test, the sample shows a smooth surface, which was roughened by partial pullout of dispersed phases during sliding test. EDS and XRD analysis confirmed that the material comprised mainly three phases: alpha-Al₂O₃ as the matrix phase (the darkest, continuous phase), with dispersed ZnAl₂O₄ (the brightest), and an acicular complex oxide phase of ZnO–nAl₂O₃ (n=3–9). The details of the formation mechanism on those phases can be found in a previous report. Of these dispersed phases, ZnAl₂O₄ particles have preferentially fallen out; they...
Fig. 5. SEM images of the 10 mass% ZnO-added alumina sample before (upper), and after the sliding experiment (lower).

Fig. 6. Trace of the particles falling off in 10 mass% the ZnO-added alumina sample upon sliding.

appear white in the SEM image in Fig. 5. Figure 6 shows a close-up the vicinity of a trace formed by particles falling out in a 10 mass% ZnO-added alumina sample. ZnAl\(_2\)O\(_4\), the equimolar compound of Al\(_2\)O\(_3\) and ZnO, exhibits a Mohs hardness of about 6.5. Thus, it is softer than alumina, whose Mohs hardness is 9. On the other hand, Zn–nAl\(_2\)O\(_3\) is likely to be as hard as alumina because it contains more Al\(_2\)O\(_3\) than ZnAl\(_2\)O\(_4\) does. These facts help explain why ZnAl\(_2\)O\(_4\) was worn preferentially and pulled out during the sliding test.

On the basis of the results shown in Fig. 3, it should be noted that in the case of 10 mass% ZnO-added alumina a smoother surface provides better wettability to water.

Figure 7 schematizes a liquid drop on a solid with a smooth (left) and rough surface (right). It is well known that the relationships between the surface energies of a solid (\(\gamma_S\)) and liquid phases (\(\gamma_L\)) and the interfacial energy between the solid and liquid interfaces (\(\gamma_{SL}\)) can be expressed as follows.

\[
\cos \theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad (1)
\]

On a roughened surface, the energy balance changes to,

\[
\cos \theta_f = R \cdot \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad (2)
\]

Where \(\theta\) is the contact angle of the liquid on the smooth surface, \(\theta_f\) is the apparent contact angle on the roughened surface, and \(R\) is a surface roughness factor. \(R\), which is defined as (real surface area/apparent surface area), and normally exceeds 1 (\(R > 1\)). Arithmetically, this means that if a surface is wettable (\(\theta < 90^\circ\)) (unwettable (\(\theta > 90^\circ\)), as the surface becomes rougher, it also becomes more wettable (unwettable).

Figure 8 plots the relationship between the surface roughness and water contact angle of conventional (ZnO-free) alumina. In the case of the alumina, the contact angle decreases with increasing surface roughness, which suggests that the apparent wettability of alumina was improved by roughening of the surface. This results is consistent with prediction based on the relationship between Eqs. (1) and (2).

However, as shown in Figs. 1, 2 and 3, 10 mass% ZnO-added alumina gave the opposite results. The analysis results described above suggest that the increase in frictional force of ZnO added alumina upon the long-term slide testing is attributable to the fall-out of ZnAl\(_2\)O\(_4\) particles and the consequent traction on the sliding surface. Moreover, because ZnAl\(_2\)O\(_4\) is a component that improves hydrophilic properties, its fall-out presumably increases the contact angle.

4. Conclusion

Changes in the microstructure and properties of ZnO-added alumina during sliding tests under water lubrication were studied.

(1) Although the frictional force of the 10 mass% ZnO-added alumina was lower than that of conventional alumina in the early stage, it increased after a long-term sliding test.

(2) Of the two phases dispersed in the samples, namely,
acicular ZnO–nAl₂O₃ (n = 3–9) and granular ZnAl₂O₄, the soft ZnAl₂O₄ phase was worn preferentially and fell out during testing.

3) The increase in frictional force during the sliding test was attributed to the fall-out of ZnAl₂O₄ particles and the resultant traction on the sliding surface.

References