Tribological behavior of RH ceramics made from rice husk sliding against stainless steel, alumina, silicon carbide, and silicon nitride

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ABSTRACT

The tribological behavior of rice husk (RH) ceramics, a hard, porous carbon material made from rice husk, sliding against stainless steel, alumina, silicon carbide, and silicon nitride (Si₃N₄) under dry conditions was investigated. High hardness of RH ceramics was obtained from the polymorphic crystallinity of silica. The friction coefficients for RH ceramics disks sliding against Si₃N₄ balls were extremely low (<0.1), irrespective of contact pressure or sliding velocity. Transfer films from RH ceramics formed on Si₃N₄ balls. Wear-mode maps indicated that the wear modes were powder formation under all tested conditions, resulting in low specific wear rates (<5×10⁻⁹ mm³/N).

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1. Introduction

The annual global production of rice is more than 650 million tons [1,2], and the main by-products of rice milling are rice husk and rice bran. Each ton of paddy rice yields approximately 220 kg of rice husk. Both rice husk and rice bran are rich in organic compounds such as cellulose and lignin, but only rice husk is rich in amorphous silica (15–22 mass% of the rice husk) [3–5]. Because of such a high percentage of silica blended with lignin, rice husk is resistant to biodegradation and is difficult to dispose of by conventional methods such as dumping or burning. Hence, rice husk presents an enormous disposal problem for industries worldwide and will continue to cause substantial ecological hazards until a better way to utilize it is discovered. Till date, traditional use of rice husk are related to agriculture, and a few notable industrial sectors have attempted to utilize rice husk, such as the steel industry as a lagging material, the water treatment industry as a clarifying filter, and the energy industry as biomass fuel. In contrast, Hokkirigawa et al. have developed a novel tribomaterial made from rice bran, called RB ceramics, by carbonizing a mixture of defatted rice bran and phenol resin in an inert gas atmosphere at 900 °C [6–8]. RB ceramics are a carbon-based material and show low friction and high wear resistance behavior under dry conditions. Because of the excellent tribological performance and the low cost of manufacturing, RB ceramics are used in several applications, including a dry linear bearing and a sleeve of dry stainless chains. However, the presence of silicon (Si) greatly affects the tribological performance of some Si-containing tribomaterials, such as silicon nitride (Si₃N₄) and Si-containing diamond-like carbon [9–15].

As an efficient use of rice husk, the development of a novel tribomaterial based on rice husk was considered to be promising. Therefore, rice husk ceramics, called RH ceramics, have been developed [16]. RH ceramics are manufactured by a two-stage carbonization of a mixture of rice husk and phenol resin in an inert gas atmosphere which is based on the RB ceramics preparation process. RH ceramics are a hard, porous carbon material containing silica. In a previous study, the tribological behavior of an RH ceramics disk against an austenitic stainless steel ball under dry and water-lubricated conditions was investigated [17]. The experimental results showed that RH ceramics show lower friction coefficients (<0.11) and lower specific wear rate (<1.5×10⁻⁹ mm³/N) under dry conditions. Slightly higher friction and wear were obtained under water-lubricated conditions. Furthermore, the effects of first-stage carbonization temperature on the friction and the wear behavior of an RH ceramics disk against a stainless steel ball were investigated [18]. RH ceramics manufactured at a first-stage carbonization temperature of 900 °C demonstrate superior tribological behavior than those manufactured at 900 °C, 1400 °C and 1500 °C. In addition, the effects of counterpart materials were revealed in another study [19]. Compared to alumina (Al₂O₃) balls, when sliding against high carbon–chromium bearing steel balls and austenitic stainless steel balls, RH ceramics manufactured at the first-stage carbonization
temperature of 900 °C display superior properties, such as low frictions (< 0.11) and low specific wear rates (< 1.0 x 10^{-8} mm²/N). As described above, RH ceramics manufactured at first-stage carbonization temperature of 900 °C have been expected to be utilized as a dry sliding material against steel materials. However, with increasing carbonization temperature, they exhibit the graphitization of amorphous carbon and the crystallization of amorphous silica [19]. Therefore, RH ceramics carbonized at high temperatures will have low friction and low wear against hard materials. The effect of specific counterpart materials on the tribological behavior of RH ceramics carbonized at high temperatures remains unclear, and these are important issues to address for the further development of RH ceramics.

For these reasons, the aims of this study were to investigate the tribological behavior of RH ceramics carbonized at 1400 °C sliding against hard stainless steel and several ceramics under dry conditions, and to discuss the low-friction mechanism.

2. Experimental details

2.1. Material preparation

Fig. 1 shows a schematic diagram of the manufacturing process of RH ceramics. First, milled rice husk powder was mixed with liquid phenol resin. The mass fractions of milled rice husk and liquid phenol resin were 75 mass% and 25 mass%, respectively. Then, the powder mixture was dried at 150–180 °C. After drying, the dried mixture was carbonized in an argon atmosphere. The first-stage carbonization temperature ($T_1$) was 400 °C. The carbonized mixture was crushed and screened to a mean particle size of less than 150 μm. Subsequently, the carbonized powder (75 mass%) was mixed again with powdery phenol resin (25 mass%). Then, the mixture was pressed at 100 °C into a disk shape. The molding pressure was 19.6 MPa, and the pressing time was 5 min. Finally, the molded disk was re-carbonized in a furnace at 1400 °C ($T_2$) in an argon atmosphere. The temperature of the furnace was raised to 500 °C at a heating rate of 30 °C/h, followed by 60 °C/h to reach the maximum temperature and held for 2 h. Then, the furnace was cooled to 600 °C at a cooling rate of 30 °C/h, followed by natural cooling.

2.2. Microstructural analysis and mechanical property testing

The microstructural morphologies of RH ceramics samples were observed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy. Raman spectroscopic analysis was used for the carbon characterization of RH ceramics. Raman spectra were obtained using a micro-Raman spectrophotometer system. X-ray diffraction (XRD) analysis was used to characterize the phase of the constituents of RH ceramics. The XRD patterns were collected using Cu Kα radiation.

Mechanical properties of RH ceramics such as density, elasticity, hardness, and surface roughness were measured. The bulk density was obtained as a ratio of the measured weight and the bulk volume of the samples. The compression tests were conducted using a uniaxial compression testing apparatus to obtain Young’s modulus. RH ceramics samples were cut to 4.9 mm × 5.0 mm × 4.9 mm size, with flat end. The rate of loading of the compression tests was 0.01 mm/s. The hardness values of RH ceramics were determined by micro-Vickers indentation method under the load of 0.98 N, the loading time of 20 s, and the number of measurements of 20 data points. The values of surface roughness were measured using a profilometer.

2.3. Tribological testing

Friction tests were conducted using a ball-on-disk-type friction tester under dry conditions in a laboratory. Fig. 2 illustrates the testing apparatus, which consisted of a moving stage, an arm with a ball holder, and a controller. A disk specimen was attached to the underside stage. A ball specimen was fixed to the upper arm with a ball holder. Then, the stage was moved linearly and perpendicularly against the arm. RH ceramics samples were used in the form of disk specimens. High carbon martensitic stainless steel (JIS SUS440C), Al₂O₃, SiC, and Si₃N₄ were used as ball specimens. Table 1 lists the mechanical properties of the ball specimens. Before each sliding test, the ball and the disk specimens were ultrasonically cleaned in hexane for 5 min, and then dried under a low-vacuum atmosphere.

Table 2 lists the experimental conditions. Each test was conducted with a constant ball specimen having a radius of 4 mm. The normal loads were 1.0, 2.0, 4.9, and 9.8 N. The sliding velocities were 1, 5, and 10 mm/s. Each test was conducted for 2 × 10⁴ cycles of repeat passages under dry conditions with a laboratory temperature of 22 °C and relative humidity of 46%.

Friction force was measured using a load cell coupled to the upper arm, and each friction coefficient was calculated on the basis of the friction force. The values of wear volume and specific wear rate for each disk specimen were calculated on the basis of

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![Figure 1](image_url)  
**Fig. 1.** Manufacturing process for RH ceramics.
3. Results and discussion

3.1. Microstructural characterization and mechanical property

Fig. 3 shows SEM images and the elemental mappings of RH ceramics. The elemental mapping of Si closely corresponded to that of oxygen. Therefore, the main constituents of RH ceramics were considered to be carbon and silica.

Fig. 4 shows the Raman spectra of RH ceramics. Two broad band peaks at approximately 1360 cm\(^{-1}\) and 1590 cm\(^{-1}\) were observed for each sample and were called the D-band and G-band, respectively. Thus, the carbon phase of RH ceramics had an amorphous structure.

Fig. 5 shows the XRD patterns of RH ceramics. The XRD pattern of RH ceramics carbonized at 1400 °C showed a sharp peak at approximately 21°, characteristic of a polymorphic crystal of silica (cristobalite), superimposed on a broad background induced by the remaining amorphous carbon and silica [20,21]. Moreover, the pattern of RH ceramics carbonized at 1400 °C featured a sharp peak at approximately 36°, implying the formation of a small amount of silicon carbide (SiC). In comparison, RH ceramics carbonized at 900 °C showed no evidence of the formation of a crystalline phase.

Table 3 lists the mechanical properties of RH ceramics. RH ceramics displayed lower values of bulk density than graphite or glassy carbon. Volatile silicon monoxide and carbon monoxide are produced in a chemical reaction of silica and carbon contained in rice husk material carbonized at 1400 °C [22]. The volatile reactants decrease the bulk density of RH ceramics. In addition, RH ceramics displayed approximately the same value of Young’s modulus as that by quenching steel. The high hardness was attributed to hard cristobalite.

3.2. Friction and wear properties of RH ceramics

Fig. 6 shows the typical friction coefficient variation of RH ceramics at a normal load of 1.96 N and a sliding velocity of 5 mm/s. The friction coefficients for RH ceramics sliding against each ball type rapidly decreased during the initial stage of friction. Then, RH ceramics sliding against SiC balls displayed stable friction coefficients (approximately 0.15). Friction coefficients for RH ceramics sliding against the stainless steel and Si\(_3\)N\(_4\) balls showed a further decrease. In contrast, the friction coefficients for RH ceramics sliding against Al\(_2\)O\(_3\) balls increased gradually and exceeded 0.18.

Fig. 7 shows the relationship between the friction coefficients for RH ceramics at 2 \(\times\) 10\(^4\) cycles and the sliding velocities. RH ceramics sliding against the stainless steel balls had extremely low friction coefficients (< 0.10) at low-contact pressures, as shown in Fig. 7(a). Fig. 7(b) shows that the friction coefficients for RH ceramics sliding against Al\(_2\)O\(_3\) balls were relatively high (> 0.10) under a wide range of contact pressures and sliding velocities. In particular, the friction coefficients exceeded 0.14 at low-contact pressures. The friction coefficients between RH ceramics and SiC balls increased with both increasing contact pressure and sliding...
velocity and exceeded 0.18, as indicated in Fig. 7(c). Conversely, RH ceramics sliding against Si₃N₄ balls showed extremely low friction coefficient values under all test conditions.

Fig. 8 illustrates the relationship between the specific wear rates of RH ceramics and the sliding velocity. RH ceramics sliding against the stainless steel balls had low specific wear rates ($\leq 2 \times 10^{-9}$ mm$^3$/N), irrespective of contact pressures and sliding
velocities. The specific wear rates of RH ceramics sliding against Al₂O₃ balls were extremely low (approximately 1 × 10⁻⁹ mm²/N) at high-contact pressures, as shown in Fig. 8(b). Fig. 8(c) shows that the specific wear rates of RH ceramics sliding against SiC balls increased with increasing sliding velocity and were relatively high (> 2.5 × 10⁻⁹ mm²/N) at low-contact pressures. The increasing
tendency on specific wear rates at low-contact pressures was clearly observed for RH ceramics sliding against Si$_3$N$_4$ balls, as shown in Fig. 8(d). Although the specific wear rates of RH ceramics sliding against SiC or Si$_3$N$_4$ balls showed relatively high values, all obtained values of specific wear rate were lower than the value of $5 \times 10^{-9}$ mm$^2$/N.

3.3. Analysis on the worn surface of counterpart materials

It was demonstrated that RH ceramics carbonized at 1400 °C showed low wear against each ball material and also showed extremely low friction against the martensitic stainless steel or Si$_3$N$_4$ under dry conditions.

Fig. 9 shows the optical images of the typical appearance of the wear scarring on each ball type, which were obtained after the friction tests at a normal load of 1.96 N and a sliding velocity of 5 mm/s. The formation of some transfer films and wear debris from RH ceramics were observed on the wear scarring of the stainless steel and Si$_3$N$_4$ balls. Conversely, remarkable scratch marks were obtained on SiC balls. Al$_2$O$_3$ balls had no transfer film and no scratch marks.

Fig. 10 shows the Raman spectra in the center of the wear scar of each ball type shown in Fig. 9 and pure surfaces: (a) stainless steel and silicon nitride, and (b) alumina and silicon carbide.

Fig. 9. Optical images of the typical appearance of wear scar on each ball type at 1.96 N and 5 mm/s: (a) stainless steel, (b) alumina, (c) silicon carbide, and (d) silicon nitride.

Fig. 10. Raman spectra in the center of wear scar of each ball type shown in Fig. 9 and pure surfaces: (a) stainless steel and silicon nitride, and (b) alumina and silicon carbide.
Al₂O₃ balls. Similarly, SiC is a chemically stable material. Si₃N₄ is also a stable material, but has compatibility with the mixtures of carbon/silica.

Although the transfer films affected the friction behavior of RH ceramics, the specific wear rates were low (≤ 5 × 10⁻⁹ mm²/N), irrespective of the transfer film. Because RH ceramics are hard and brittle materials, wear of RH ceramics will be dominated by brittle fracture. Hokkirigawa reported that wear modes of ceramics are distinguished as three types, which are flake formation mode accompanied with large brittle fracture, powder formation mode accompanied with microcracks, and plowing mode accompanied with no brittle fracture [23]. Each wear mode correlates to the values of wear coefficient (K), which is the product of hardness and specific wear rate, and can be classified by the coefficients briefly as follows [23].

Flake formation: \( K = 10^{-2} \)– 10⁻¹
Powder formation: \( K = 10^{-3} \)– 10⁻²
Plowing: \( K < 10^{-5} \)

RH ceramics had 10⁻⁶–10⁻⁴ of wear coefficients in this study. Therefore, the wear modes of RH ceramics were considered as powder formation or plowing.

In addition, Hokkirigawa proposed wear-mode maps for ceramics using linear fracture mechanics [23]. On the basis of the wear-mode maps, a dimensionless parameter \( S_c \) and a critical parameter \( S_{c, \text{critical}} \) can be calculated by the following equations:

\[
S_c = \frac{P_{\text{max}} \sqrt{R_{\text{max}}}}{K_{\text{f}}}
\]

\[
S_{c, \text{critical}} = \frac{7}{1 + 10 \mu}
\]

where \( P_{\text{max}} \) is the Hertzian maximum contact pressure [Pa], \( R_{\text{max}} \) is the maximum surface roughness [m], \( K_{\text{f}} \) is the fracture toughness [Pa·m], and \( \mu \) is the friction coefficient. \( S_c \) expresses the severity of contact. \( S_{c, \text{critical}} \) is the approximate expression based on several numerical calculations [23]. If \( S_c \) is smaller than \( S_{c, \text{critical}} \), wear modes are determined as powder formation or plowing modes.

Fig. 11 shows the wear-mode map of RH ceramics, in which the early-stage friction coefficients and the surface roughness of the pure surface were chosen. The value of the fracture toughness of RH ceramics was calculated based on the reference data in other literature [22]. The \( S_c \) of RH ceramics was smaller than \( S_{c, \text{critical}} \) under all tested conditions during the initial stage of friction. Thus, the initial wear mode of RH ceramics was powder formation or plowing. In addition, powder formation and plowing can be distinguished using a dimensionless parameter \( S_c \) and a critical parameter \( S_{c, \text{critical}} \).

\[
S_{c, \text{critical}}^* = \frac{5}{1 + 10 \mu}
\]

where \( H_v \) is the Vickers hardness of RH ceramics [Pa]. The initial wear mode of RH ceramics was determined as powder formation under all tested conditions, as demonstrated in Fig. 12(a). Furthermore, the wear-mode map at 2 × 10⁴ cycles was constructed, as shown in Fig. 12(b). In the map, all plots moved near the transition curve to plowing. In particular, the plots for RH ceramics sliding against stainless steel or Al₂O₃ balls were nearer than SiC or Si₃N₄ balls. Therefore, RH ceramics sliding against SiC and Si₃N₄ balls showed relatively higher wear than the other counterpart materials. Nevertheless, these results from the wear-mode maps indicated that the wear mode of RH ceramics was powder formation accompanied with microcracks under all tested conditions in this study, resulting in low wear (≤ 5 × 10⁻⁹ mm²/N). Indeed, the observation of the worn surfaces revealed that the catastrophic wear of RH ceramics accompanied by large brittle fracture was prevented overall, as shown in Fig. 13.

4. Conclusions

(1) RH ceramics carbonized at 1400 °C sliding against stainless steel balls showed extremely low friction coefficients (≤ 0.10) at low-contact pressures under dry conditions. Furthermore, the extremely low friction coefficients were obtained for RH ceramics at all tested conditions when the counterpart material was Si₃N₄.

(2) The specific wear rates of RH ceramics tended to decrease with increasing contact pressure and decreasing sliding velocity, irrespective of the counterpart material. Although Si₃N₄ balls induced the highest specific wear rates of RH ceramics among other materials, the values were low (≤ 5 × 10⁻⁹ mm²/N).
A transfer film from RH ceramics was an important factor for achieving a low friction coefficient ($<0.10$).

Wear-mode maps of RH ceramics indicated that a catastrophic wear of RH ceramics accompanied by large brittle fracture was prevented. Therefore, RH ceramics had low wear against each tested ball material.

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