Short Communication

Tribological Behavior of Cast Iron in Ethanol with and without Oleic Acid

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The tribological behavior of cast iron was investigated by sliding a disk against a bearing steel pin in ethanol, with and without oleic acid, using a pin-on-disk machine. The addition of oleic acid resulted in decreased friction in ethanol. The profile of the wear track was measured using a surface texture and contour measurement instrument. Microstructural observations and chemical analysis of the worn surface were performed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. The results indicated that mechanical wear such as plowing and adhesion occurred on the sliding surface of the cast iron in ethanol. In addition, galvanic corrosion was identified as a possible main cause for the removal of the cast iron material by sliding in ethanol with oleic acid.

Keywords: cast iron, bearing steel, ethanol, oleic acid, friction, wear, corrosion

1. Introduction

Ethanol is utilized as a renewable biomass fuel but is widely different from petroleum fuel in terms of its physical and chemical properties. Therefore, it is difficult to use ethanol fuel in conventional systems designed for petroleum fuel. One serious problem is the corrosion of materials in contact with ethanol fuel. Ferrous materials used for transportation pipelines and storage tanks exposed to ethanol fuel are subjected to corrosion such as pitting corrosion and stress corrosion cracking [1-3]. Many research groups have investigated the mechanism for corrosion of ferrous materials in ethanol. Recently, it was reported that acetic acid (CH_3COOH), which is a monovalent short-chain carboxylic acid, accelerates the electrochemical corrosion of ferrous materials in ethanol [1,4,5]. Goodmann et al. reported that the addition of acetic acid to fuel-grade ethanol resulted in inhibition of the repassivation of steel [4]. Samusawa et al. reported that acetic acid caused breakage of the oxide layer that acts as a passivation film on carbon steel in fuel-grade ethanol [5]. The pitting corrosion of carbon steel occurred as a result of the anodic dissolution of iron [5].

We have investigated the tribological characteristics of candidate sliding materials for ethanol fuel engines. Iron based materials such as steel and cast iron are widely used for piston rings and cylinder linings [6]. We have previously reported that adhesive wear occurs on the surfaces of SUS440C stainless steel disks and an FC250

cast iron disks slid against a SUS440C stainless steel pin in ethanol [7,8].

In automotive engines, pistons and cylinders slide in a mixed atmosphere of fuel and engine oil [9]. The engine oil contains an oiliness agent to reduce wear on the engine components. Oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$), which is a typical oiliness agent, is a monovalent long-chain carboxylic acid that dissociates into the carboxylate anion and a proton [10]:

The carboxylate anion is solvated by protic polar solvents such as ethanol [10]. In ethanol, the dissociation of carboxylic acid proceeds because the carboxylate anion is stabilized by solvation [10]. Therefore, oleic acid is considered to not only act as an oiliness agent but also as an electrolyte in ethanol. By analogy with acetic acid, oleic acid may thus influence the electrochemical corrosion behavior of ferrous materials.

We also investigated the effect of oleic acid addition on the friction and wear behavior of stainless steel in ethanol [8]. Iron oleate was formed on the sliding surface of stainless steel by the tribochemical reaction between iron and oleic acid [8]. Removal of the iron oleate by sliding caused tribochemical wear [8]. For a stainless steel surface in ethanol containing oleic acid, the oleic acid caused a chemical reaction rather than electrochemical corrosion.

The carbon content of cast iron is higher than that of steel, and graphite is crystallized in the iron base in a cast iron structure. The cast iron tends to form local cells where iron metal acts as an anode and graphite acts as a cathode [11]. Therefore, cast iron may be more sensitive to the electrolyte action of a long-chain carboxylic acid than steel. To use ethanol as a fuel, it is thus necessary to determine the sliding characteristics of cast iron in ethanol containing a long-chain carboxylic acid.

In this investigation, a cast iron disk was slid against a bearing steel pin in ethanol with and without oleic acid. We discuss the effects of oleic acid on the tribological behavior of the cast iron with respect to the friction coefficient, the specific wear rate, and the results of a morphological and chemical analysis of the worn surface.

2. Experimental procedure

Sliding tests were performed using a pin-on-disk unidirectional machine [12]. The lubricants employed were dehydrated ethanol (C_2H_5OH , 99.5%, $H_2O < 50$ ppm), with and without oleic acid. The concentration of oleic acid in the ethanol solution was 5 mass%. The viscosities of pure ethanol and the ethanol solution of oleic acid were 1.083 and 1.106 mPa·s, respectively. The relative permittivities of pure ethanol and the ethanol solution of oleic acid were 24.8 and 23.9, respectively. An FC250 cast iron disk (1.9 GPa Vickers hardness, 5 mm thick, 20 mm diameter) was slid against a SUJ2 bearing steel hemispherical pin (3.3 GPa Vickers hardness, 2 mm hemisphere radius) in the lubricant. The applied load was 0.735 N, the sliding speed was 40 mm/s and the sliding distance was 240 m. Sliding tests were conducted in dry air with a relative humidity of less than 20%. Each test was run three times. After the sliding test, both the disk and pin were washed with petroleum ether, acetone and ethanol, and then air-dried. The profile of the wear track was then measured using a surface texture and contour measurement instrument. Microstructural observations and chemical analysis of the worn surface were performed using scanning electron microscopy (SEM; accelerating voltage: 6 kV) and energy-dispersive X-ray spectroscopy (EDS; accelerating voltage: 15 kV).

The wear volume of the disk was approximated by the product of the mean area of 10 cross sections of a wear track and the circumferential length of the wear track. The wear volume of the pin ($V(\text{pin})$) was approximated by [13]:

$$V(\text{pin}) = \frac{\pi d^4}{64r} \quad (2)$$

where d is the wear scar diameter and r is the radius of the hemispherical pin (2 mm).

SEM images of the unworn surfaces of the tested materials are shown in Fig. 1. The dark grey areas are graphite and the light grey areas are mainly iron in the cast iron disk (Fig. 1(a,c)). The grooves on the surface of

Fig. 1 SEM images of unworn surfaces of (a) FC250 cast iron disk, (b) SUJ2 bearing steel pin, (c) magnified view of (a) and (d) magnified view of (b)

the bearing steel pin were most likely formed during polishing of the samples (Fig. 1(b,d)).

3. Results and discussion

3.1. Friction and wear behavior

Figure 2 shows the average friction coefficient as a function of the sliding distance, where the error bars represent the standard deviation. The addition of oleic acid to ethanol resulted in a decrease in friction.

Figure 3 shows 3D profiles of a part of the wear tracks from the cast iron disks sliding against the bearing steel pin. The wear tracks in ethanol were groove shaped (Fig. 3(a)), whereas the surface of the cast iron disk worn

Fig. 2 Friction coefficients in ethanol and in ethanol solution of oleic acid as a function of sliding distance

Fig. 3 3D profiles of wear tracks of cast iron disks slid against a bearing steel pin; (a) wear track in ethanol, and (b) wear track in ethanol solution of oleic acid

* Wear of cast iron disk in ethanol solution of oleic acid could not be calculated.

Fig. 4 Specific wear rate for cast iron disk and bearing steel pin worn in ethanol and in ethanol solution of oleic acid

in an ethanol solution of oleic acid was dotted with hollows (Fig. 3(b)).

Figure 4 shows the specific wear rate for the cast iron disk and bearing steel pin. The specific wear rate for the bearing steel pin was $5.1 \times 10^{-7} \text{ mm}^3/(\text{Nm})$ both in ethanol and in an ethanol solution of oleic acid, while that for the cast iron disk in ethanol was as high as $1.3 \times 10^{-5} \text{ mm}^3/(\text{Nm})$. The wear volume of the cast iron disk in an ethanol solution of oleic acid could not be calculated using the cross-sectional area of the wear track.

3.2. SEM and EDS analysis of worn surfaces

3.2.1 Surfaces worn in ethanol

Figure 5 shows SEM images and EDS maps of the cast iron disk worn in ethanol. On the surface, a groove along the sliding direction, plastic deformation and pits formed by adhesion were observed (Fig. 5(a,b)). After sliding, the abundance of C on the disk surface was reduced (Fig. 5(c)) because the plastically deformed iron covers the graphite on the surface during the sliding process. Sliding resulted in an increase of O on the surface because the highly reactive nascent surface

formed by adhesion reacts with dissolved oxygen in ethanol to form iron oxides. SEM observations and EDS analyses suggested that plastic deformation and adhesive wear occurred on the cast iron disk surface when slid against the bearing steel pin in ethanol.

Figure 6 shows SEM images of the bearing steel pin surface worn in ethanol, where spread adhesive substances and pits were observed (Fig. 6(a,b)). The adhesive substances may originate from the cast iron disk and the pits may be formed by adhesion.

Fig. 5 SEM images and EDS maps of cast iron disk surface worn in ethanol. (a) SEM image, and (b) magnified view of (a). (c) C, (d) O, and (e) Fe maps. Bold arrows in (a) and (b) indicate the sliding direction. The concentration of each component in (c), (d) and (e) is expressed in terms of the brightness

Fig. 6 SEM images of bearing steel pin worn in ethanol; (a) wear scar and (b) magnified image of (a). Bold arrows indicate the sliding direction

Fig. 7 SEM images and EDS maps of cast iron disk surface worn in ethanol solution of oleic acid. (a) SEM image, and (b) magnified view of (a). (c) C, (d) O, and (e) Fe maps. Bold arrows indicate the sliding direction in (a) and (b). The concentration of each component in (c), (d) and (e) is indicated by the brightness

3.2.2 Surfaces worn in an ethanol solution of oleic acid

Figure 7 shows SEM images and EDS maps of the cast iron disk surface worn in an ethanol solution of oleic acid, where many hollows were observed (Fig. 7(a,b)). These hollows were not observed on the unworn surface of the cast iron disk (Fig. 1(a,c)). Away from these hollows, the surface was smooth. EDS analysis revealed that high C concentration areas were dispersed inside the wear track (Fig. 7(c)).

Figure 8 shows magnified SEM image and EDS maps of the cast iron disk surface worn in an ethanol solution of oleic acid. Material removal occurred in the vicinity of the high C concentration area. The proportions of C, O, Si and Fe in the high C concentration areas (point 1 in Fig. 8(a)) were 96.36, 0.56, 0.15 and 2.92 at%, respectively. Therefore, the flakes in these areas were graphite. The results indicated that dissolution of the iron occurred preferentially in the vicinity of graphite flakes on the sliding surface of the cast iron disk.

Figure 9 shows SEM images of the bearing steel pin worn in an ethanol solution of oleic acid. Many adhesive substances (black areas in Fig. 9) were observed on the smooth worn surface. The smoothness of the worn surface suggests that tribochemical wear occurred on the bearing steel pin surface during sliding. The concentration of C in an area with an adhesive substances

Fig. 8 (a) SEM image and EDS (b) C, (c) O, and (d) Fe maps of cast iron disk surface worn in ethanol solution of oleic acid. The concentration of each component in (b), (c) and (d) is indicated by the brightness

Fig. 9 SEM images of bearing steel pin worn in ethanol solution of oleic acid; (a) wear scar, and (b) magnified image of (a). Bold arrows indicate the sliding direction

(point 2 in Fig. 9(a), chemical composition; C 41.40 at%, O 3.12 at%, Si 0.29 at%, Fe 55.20 at%) was higher than that in an area without an adhesive substances (point 3 in Fig. 9(a), chemical composition; C 14.05 at%, O 1.68 at%, Si 0.32 at%, Fe 83.95 at%), which indicated that the attached substances originated from oleic acid and/or graphite in the cast iron.

3.3. Proposed mechanism for material removal

3.3.1 Proposed mechanism for material removal in ethanol

The wear track in ethanol was groove shaped (Fig. 3(a)). Plastic deformation of the cast iron disk, adhesive substances on the bearing steel pin and pits on both the cast iron disk and bearing steel pin were observed (Figs. 5 and 6). These results suggest that mechanical wear such as plowing of the cast iron disk by the bearing steel pin

and adhesive wear occur on the sliding surface between the cast iron disk and bearing steel pin in ethanol.

3.3.2 Proposed mechanism for material removal in ethanol solution of oleic acid

The surface of the cast iron disk was dotted with hollows (Fig. 3(b)). SEM observation and EDS analysis of the worn disk indicated that the hollows were formed by the dissolution of iron in the vicinity of graphite flakes. The hollows were concentrated in the wear track. Figure 10 shows the proposed mechanism for hollow formation on the sliding surface. Iron-carboxylate is formed by chemisorption and/or reactions of long-chain fatty acids on the surface of the iron-based materials [8,14-19]. Before sliding, the surface of the disk was covered with iron oleate layer and iron oxide layer, which acted as a boundary lubrication film and a passivation film, respectively [5,14,15]. The iron oleate is removed from the surface of the iron-based materials by sliding [16]. Mechanical stress and scratching has been reported to break the passivation film on iron-based metal and cause local corrosion [4,20]. In the present work, breakage of the iron oleate lubrication film and the iron oxide passivation film occurs during sliding. Bare iron metal is then exposed to the lubricant at the place where the passivation film is broken. In the ethanol solution, oleic acid acts as an electrolyte as well as an oiliness agent. A local cell, where iron metal acts as an anode and graphite acts as a cathode, is formed on the surface of the cast iron disk [5,11,21]. Galvanic corrosion between iron and graphite then occurs on the cast iron disk. The anodic dissolution of iron, in which Fe^{2+} ions dissolve into the ethanol solution, occurs in the vicinity of graphite flakes. The Fe^{2+} ions are stabilized by oleate ions ($\text{C}_{17}\text{H}_{33}\text{COO}^-$) to form iron oleate

Fig. 10 Proposed mechanism for hollow formation on sliding surface of cast iron disk in ethanol solution of oleic acid

(($\text{C}_{17}\text{H}_{33}\text{COO}$) $_2\text{Fe}$) in the ethanol solution [5]. The anodic dissolution of iron results in the formation of hollows. Galvanic corrosion could thus be the main cause for the removal of the cast iron disk material when worn in an ethanol solution of oleic acid. In order to evaluate the galvanic corrosion quantitatively, detailed electrochemical studies are needed.

In contrast, the surface of the bearing steel pin worn in the ethanol solution of oleic acid was smooth. Under the sliding conditions, iron oleate formed by chemisorption and/or reaction of oleic acid is removed evenly from the bearing steel pin surface [8,16,17]. It is considered that the main mechanism for material removal from the bearing steel pin in the ethanol solution of oleic acid is thus tribochemical wear.

Iron oleate has a lubricating effect because of its high viscosity [18,19]. In an ethanol solution of oleic acid, iron oleate could be formed by electrochemical and tribochemical reactions and chemisorption in sufficient amounts to act as a lubricating film. Furthermore, the hollows on the wear track of the cast iron disk can act as oil sumps. Thus, iron oleate would contribute to a reduction of friction and inhibit adhesion and plowing on the sliding surface between the cast iron disk and bearing steel pin in an ethanol solution of oleic acid.

4. Summary

The experimental results and proposed mechanisms for material removal are summarized here.

- 1) On the sliding surface between the cast iron disk and bearing steel pin in ethanol, mechanical wear such as plowing of the disk by the bearing steel pin and adhesive wear occurs.
- 2) In an ethanol solution of oleic acid, oleic acid acts as an electrolyte as well as an oiliness agent. A local cell, where iron metal acts as an anode and graphite acts as a cathode, could form on the surface of the disk. Galvanic corrosion between iron and graphite would then cause the formation of hollows on the sliding surface.
- 3) The main mechanism for material removal from the bearing steel pin in an ethanol solution of oleic acid is tribochemical wear, whereby tribochemically formed iron oleate is removed evenly from the surface.
- 4) The iron oleate formed contributes to a reduction of friction and inhibits adhesion and plowing on the sliding surface between the cast iron disk and bearing steel pin in an ethanol solution of oleic acid.

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