Tribological performances of halogen-free ionic liquids against a-C:H and ta-C films under vacuum

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Abstract
Ionic liquids have high potential as novel lubricants because of their unique physical properties. In particular, halogen-free ionic liquids are low environmental-load lubricants. Unfortunately, these ionic liquids exhibit a poor tribological performance against bearing steel. However, they exhibit high performances against diamond-like carbon (DLC) under the high vacuum condition. The influence of DLC species on tribological performances and the reaction mechanism of halogen-free ionic liquids on the worn surface are still unknown. This investigation evaluates the tribological performances of halogen-free ionic liquids (1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCN]), 1-ethyl-3-methylimidazolium tricyanomethane ([EMIM][TCC]), and 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB])) against two types of DLC (tetrahedral amorphous carbon (ta-C) and hydrogenated amorphous carbon (a-C:H)). The tribological performances of ionic liquids differed by the anion structure and the type of DLCs. The DLCs lubricated with [EMIM][DCN] and ta-C lubricated with [EMIM][TCC] exhibited a low friction coefficient. On the other hand, other ionic liquids exhibited the high friction coefficients against DLCs. A time-of-flight secondary-ion mass spectrometer analysis indicated that the tribo-decomposition of halogen-free ionic liquids and the adsorption of anion achieve a low friction. The chemical activity of nascent surfaces plays a very important role in achieving tribo-decomposition. However, because this activity of DLC was lower than that of bearing steel, [EMIM][TCC] exhibited a poor tribological performance. Thus, although the tribological performances of halogen-free ionic liquids can be improved by using DLC as sliding materials, there is also the possibility of inhibiting the formation of an adsorption layer derived from ionic liquids.

Keywords: Tribology, Ionic liquids, Diamond-like carbon, Vacuum, ToF-SIMS

1. Introduction

Usually, the term “liquid” refers to molecular liquids such as water or alcohol. However, ionic liquids can form a liquid phase at a temperature less than 100 °C despite containing salts, which consist of cations and anions, (Walden, 1914). These liquids have high potential as lubricants because of their fascinating properties, such as low vapor pressure, non-volatility, and non-combustibility, (Wilkes, 2002). In addition, these properties can be controlled by the combination of ions, (Zhou et al., 2009). An important physical property of ionic liquids is that it is difficult to dissolve ionic liquids in a base oil. It has been reported that the kind of cation dramatically increases the solubility of the ionic liquid in the base oil. Therefore, in recent years, investigation of ionic liquids as additives has also increased, (Zhou et al, 2017). However, the reasons behind the tribological performances and the lubricating mechanism when using ionic liquids are unclear.

Generally, the tribological performances of ionic liquids have been investigated against steel materials. Halide anions are reported to exhibit high tribological performances and may be superior to the existing lubricating oils, such as poly-α-olefin, phosphorus extreme pressure agent, and perfluoropolyether (Ye, et al., 2001). In addition, the low wear volume of halide anions are also reported. It is considered that the metal halide formed by sliding achieve the low friction and wear volume (Suzuki, et al., 2007), (Philips, et al., 2007). However, a high compensation that involves corrosion of the
steel materials is required (Kondo et al., 2012), (Watanabe et al., 2013). It is very interesting that the corrosion progresses not only during sliding but also after the sliding test. In addition, hydrogen fluoride, which is a toxic gas, may form during the tribochemical reaction of halide anions on the worn surface (Swatloski et al., 2003). Therefore, it is necessary to use halogen-free ionic liquids from the viewpoint of environment and safety.

However, unfortunately, even though halogen-free ionic liquids do not generate toxic gases, they exhibit poor tribological performances against steel materials as compared with halogen-based ionic liquids (Minami et al., 2011). About sliding tests against steel materials, halide anions exhibit low friction coefficient of less than 0.1 under the room temperature. On the other hand, friction coefficients of halogen-free ionic liquids often show more than 0.1. It is not uncommon to show almost the same friction coefficient as a conventional base oil. In addition, wear is large. Thus, it is necessary to improve the tribological performances of halogen-free ionic liquids. One effective means is to synthesize new ionic structures (Kawada et al., 2018a). It is thought that anions adsorb on to the worn surfaces to bring about low friction of less than 0.1. However, the problem of wear resistance remains, and the number of structural species of halogen-free ionic liquids is limited. Especially, the specific wear rate of halogen-free ionic liquids is very large even with low friction (Kawada et al., 2018b). Another effective means is to use sliding materials made of hard materials (Kawada et al., 2017a), (Kondo et al., 2013). Ceramics, nitrogen coating, and diamond-like carbon (DLC) improve the tribological performances of halogen-free ionic liquids. In particular, halogen-free ionic liquids exhibit high tribological performances against tetrahedral amorphous carbon films, which are DLCs, under the high vacuum condition (Kawada et al., 2017b). However, the influence of DLC species on tribological performances and the reaction mechanism of halogen-free ionic liquids on the worn surface are still unknown.

This investigation evaluates the tribological performances of halogen-free ionic liquids against two types of DLCs. To understand the effects of anion components on tribological performances, three types of halogen-free ionic liquids were used as lubricants. In addition, the details of the reaction mechanism on the worn surface are discussed using a time-of-flight secondary-ion mass spectrometer (ToF-SIMS).

Table 1  Chemical structures of the used ionic liquids.

| Chemical Structure | Name                                      |
|--------------------|-------------------------------------------|
| ![Image](image1)   | 1-ethyl-3-methylimidazolium dicyanamide   |
| ![Image](image2)   | 1-ethyl-3-methylimidazolium tricyanomethane |
| ![Image](image3)   | 1-ethyl-3-methylimidazolium tetracyanoborate |

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2. Experimental details

2.1 Experiment

The sliding tests were conducted under vacuum conditions using a ball-on-disk friction tester (Kawada et al., 2014). Both the specimens and jig were ultrasonically cleaned twice with a mixed solution of petroleum benzine and acetone in a ratio of 1:1 for 20 min. The operating parameters for the sliding tests were as follows: the degree of vacuum was $2.0 \times 10^{-5}$ Pa, the tests were conducted at room temperature, the amount of lubricants was 30μL, the load was 3.5 N, sliding velocity was 52.3 mm/s, and the test duration was 60 min. All the sliding tests were repeated ten times, and the test results revealed good reproducibility. The images of the worn surfaces after the sliding tests were obtained by laser microscopy (VK-X 150, Keyence, Japan). This microscopy measured the wear scar diameter and wear volume of each specimens.

2.2 Materials

The chemical structures of the halogen-free ionic liquids used as lubricants in this investigation are listed in Table 1. Three kinds of halogen-free ionic liquids were used: 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCN]), 1-ethyl-3-methylimidazolium tricyanomethane ([EMIM][TCC]), and 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB]). All halogen-free ionic liquids were commercial lubricants synthesized by Merck Chemicals (Germany). Detailed information on the used ionic liquids are listed in Table 2. The viscosities and decomposition points were measured using a tuning-fork vibration viscometer (SV-1A, A&D Company, Japan) and a thermogravimetric analysis unit (TG-DTA2010SA, Bruker, USA), respectively (Kawada et al., 2018a). The decomposition points were defined as that at which 5% weight loss occurred.

The ball specimen was 4 mm in diameter. The disk specimen was 24 mm in diameter and 7.9 mm in thickness. Both specimens were made of bearing steel (AISI 52100, HV 700). The following two types of DLCs were coated on the disk specimens as hard coating materials: tetrahedral amorphous carbon (ta-C) and hydrogenated amorphous carbon (a-C:H). Both DLCs were commercial coating produced by ITF Co. (Kyoto, Japan). The physical properties of DLCs are listed in Table 3. The hardness and coating thickness were measured using a triboindenter (Ti950, Hysitron, USA) and a coating thickness analyzer (Calotest, Anton Paar Tritec SA, Switzerland), respectively.

| Lubricants | [EMIM][DCN] | [EMIM][TCC] | [EMIM][TCB] |
|------------|-------------|-------------|-------------|
| Melting point (°C) | < -50 | < -50 | 13 |
| Viscosity@25°C (mPa s) | 13.77 | 14.06 | 15.79 |
| Viscosity@40°C (mPa s) | 9.66 | 10.01 | 10.58 |
| Viscosity@70°C (mPa s) | 5.14 | 5.36 | 5.20 |
| Purity (%) | 98.0 | 98.0 | 99.5 |
| Decomposition point (°C) | 288.5 | 333.5 | 391.6 |
| Water content (ppm) | < 10000 | < 10000 | < 100 |
| Halide content (ppm) | < 1000 | < 1000 | < 100 |

| Material | ta-C | a-C:H |
|----------|------|-------|
| Method   | Arc ion plating | Unbalanced magnetron sputtering |
| DLC coating series name | HA | HP |
| Surface roughness (μm) | 0.010 | 0.005 |
| Film thickness (μm) | 1.00 | 0.65 |
| Hardness (GPa) | 73 | 10 |
| Elastic modulus (GPa) | 650 | 91 |
| Hydrogen content (%) | < 1.0 | 20.0 |
2.3 Analysis

The chemical information on worn surfaces of DLCs were analyzed using a ToF-SIMS (PHI TRIFT V Nano TOF, URVAC, USA). Before the ToF-SIMS analysis, the disk specimens were ultrasonically cleaned with a mixed solution of petroleum benzine and acetone in a ratio of 1:1 for 10 min. A pulsed electron impact ion source (30 keV, Au\(^{3+}\)) was used to generate primary ions for the analysis. The operating parameters were as follows: the analysis area was 300 \(\mu\)m \(\times\) 300 \(\mu\)m, the spatial resolution was 3 \(\mu\)m, the ion irradiation time was 4 min, the dose was \(4.09 \times 10^{10}\) ion/cm\(^2\), the measured mass range was 0.5–2000 m/e, and the mass resolution was 1955 m/\(\Delta\)m. A lateral resolution of 3 \(\mu\)m was achieved. Both positive and negative modes were used for the measurement, and both modes were taken at the same location.

3. Results
3.1 Tribological performances

Figure 1 shows the friction behavior lubricated with each halogen-free ionic liquid. Figure 2 shows the average values of the friction coefficients lubricated with each halogen-free ionic liquid for the last 5 minutes. Both DLCs lubricated with [EMIM][DCN] exhibited low friction coefficients. In addition, these friction behavior was stable. In particular, ta-C exhibited a very low friction coefficient, and this value is lower than for steel–steel contacts (Kawada et al., 2018a). For ta-C lubricated with [EMIM][TCC], the friction behavior was stable, and friction coefficient showed low value. On the other hand, in the case of [EMIM][TCC] against a-C:H, the friction coefficient showed high value. However, in the initial period (0 – 15 min.), the friction coefficient showed low value. This behavior indicates that the peeling of a-C:H was occurred at 15 minutes. With [EMIM][TCB], the friction behavior was very unstable for both DLCs, and the values was very high.

![Graph showing friction behavior of each ionic liquid against DLCs.](image)
Figure 3 shows the worn surface images of both DLC disks and bearing steel balls after the sliding tests. Figure 4 shows the wear volume of DLC disks and wear scar diameter of bearing steel balls. The wear volume was evaluated by integrating the cross-sectional area with respect to the direction of the wear track. Both DLCs lubricated with [EMIM][DCN] showed high wear resistance. However, other ionic liquids brought about the peeling of DLCs. In particular, the wear due to [EMIM][TCB] was very large. Focusing on the wear of ball, in the case of the ta-C lubricated with [EMIM][DCN], the wear scar diameter was large when compared with the case of a-C:H although the coefficient of friction was lower. On the other hand, most of the combinations where DLC peeling was observed showed a larger wear. However, a-C:H lubricated with [EMIM][TCC] showed a smaller wear. It is considered that the attack ability to bearing steel materials depends on the hardness of DLCs.

![Friction coefficient graph](image)

**Fig. 2** The average value of friction coefficient.

![Worn surface images](image)

**Fig. 3** Worn surface images of DLC disks and bearing steel balls.
3.2 ToF-SIMS analysis results

Figure 5 shows the mapping images of DLCs using ToF-SIMS. The arrow side or the location surrounded by the white line is worn surface. Color bar numbers represent intensity ratios. It has been reported that the adsorption of ions derived from halogen-free ionic liquids affects the tribological performance when steel was used as a sliding material [14]. Thus, this analysis chose the secondary ions (\([\text{EMIM}]\) cation = 111 m/e, \([\text{DCN}]\) anion = 66 m/e, \([\text{TCC}]\) anion = 90 m/e, and \([\text{TCB}]\) anion = 115 m/e) derived from the halogen-free ionic liquids. In the case of both DLCs lubricated with \([\text{EMIM}]\)[DCN], the \([\text{DCN}]\) anions adsorbed on to the worn surfaces because the intensities of the \([\text{DCN}]\) anions on the worn surface were higher than those on non-worn surfaces, and the \([\text{EMIM}]\) cations did not exist on the worn surfaces. In addition, the \([\text{DCN}]\) anions formed a uniform adsorption layer. On the other hand, the combination that showed a high friction and/or peeling of DLCs formed an island adsorption layer.

Fig. 5  The mapping images of DLCs using ToF-SIMS.
4. Discussions

From the results of sliding tests and ToF-SIMS, the tribo-decomposition of [EMIM][DCN] on the worn surface occurred because the [EMIM] cations were not detected by ToF-SIMS. In addition, the adsorption of [DCN] anions achieved a low friction. In particular, the friction coefficient of ta-C lubricated with [EMIM][DCN] was lower than that of bearing steel lubricated with the same ionic liquids (Kawada, et al., 2018a). It was reported that the adsorption of [DCN] anion itself can achieve low friction coefficient under various sliding materials (Kondo et al., 2013). In addition, the wear resistance of halogen-free ionic liquids has been considered as one of the problems. This combination achieved low attack ability to bearing steel materials, and low wear volume of DLCs were confirmed. For ta-C lubricated with [EMIM][TCC], the low friction coefficient was confirmed, but this value is higher than that lubricated with [EMIM][DCN]. The difference between these two ionic liquids is the progress of wear. It has already reported that [TCC] anion showed severe wear damage (Kondo, et al., 2013). In fact, severe damage was also caused in the a-C:H lubricated with [EMIM][TCC], and the peeling of the a-C:H was also observed. Finally, in the case of [EMIM][TCB], it has already reported that [EMIM][TCB] do not show the friction reduction effect against steel-steel contact (Minami et al., 2012). Even when DLCs used as sliding materials, [EMIM][TCB] did not have friction reduction effects. From the results of friction behavior, it is considered that the peeling of DLCs were occurred immediately after the sliding started.

[EMIM][DCN] induced adsorption of [DCN] anion on the worn surface by tribo-decomposition and achieved low friction and wear volume. From this results, the tribo-decomposition of halogen-free ionic liquids is important role. The chemical activity of nascent surfaces plays a very important role in achieving tribo-decomposition of ionic liquids because it can be said that ionic liquids undergo catalytic decomposition on the active site of the nascent surface. When bearing steel was used as the sliding material, [EMIM][DCN] and [EMIM][TCC] underwent catalytic decomposition on the nascent steel surface, and both types of anions adsorbed on to the worn surfaces (Kawada, et al., 2018a). However, it was considered that the chemical activity of DLCs are lower than those of bearing steel. Thus, [EMIM][TCC] cannot undergo catalytic degradation on the worn surfaces, and the adsorption layer will not form. Similarly, the adsorption layer of [TCB] anion derived from [EMIM][TCB] could not be formed. In the case of [EMIM][TCC] and [EMIM][TCB], there is possibility that the ionic liquid itself adsorbed on the worn surface, but this adsorption layer could not achieve low friction and wear volume. About the catalytic degradation, interionic interaction of ionic liquid is important. This interaction affects the physical properties of ionic liquids. From Table 2, [EMIM][DCN] showed lowest decomposition point and viscosity among all ionic liquids. Thus, [EMIM][DCN] achieved low friction and wear volume.

Thus, although the tribological performances of halogen-free ionic liquids can be improved by using DLCs as sliding materials, there is also the possibility of inhibiting the formation of an adsorption layer derived from ionic liquids. One solution is to use metal-doped DLCs to improve the chemical activity (Feng et al., 2012). Such DLCs can promote the tribo-decomposition of halogen-free ionic liquids. Another solution is to use cations facilitating tribo-decomposition. The thermal stability is related to tribo-decomposition. Thus, new ionic liquids should be synthesized using thermal stability as an index for tribo-decomposition. A method using an autodissociation constant as an index of thermal decomposition is used (Amyes et al., 2004), (Kütt et al., 2010). The combination of highly acidic anions and highly basic cations is believed to increase thermal stability.

5. Conclusions

The tribological performances of halogen-free ionic liquids against DLCs under the vacuum condition were evaluated. In addition, the lubricating mechanism was investigated in detail via ToF-SIMS.

(1) The tribological performances of ionic liquids were different by the anion structure and the type of DLCs. The ta-C lubricated with [EMIM][DCN] exhibited a low friction coefficient.

(2) When a low friction coefficient was confirmed, the anion itself adsorbed on to the worn surface, and the adsorption of anion required the tribo-decomposition of halogen-free ionic liquids.

(3) The chemical activity of nascent surfaces plays a very important role in achieving tribo-decomposition. Because this activity of DLC was lower than that of bearing steel, [EMIM][TCC] exhibited a poor tribological performance.
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