Tribological properties of diamond nanoparticle additive in water under a lubrication between steel plate and tungsten carbide ball

Aidil Azli ALIAS*, Hiroshi KINOSHITA* and Masahiro FUJII*
*Division of Industrial Innovation Sciences, Graduate School of Natural Science and Technology, Okayama University
3-1-1 Tsushima-naka, Kita-ku, Okayama-shi 700-8530, Japan
E-mail: kinoshita@okayama-u.ac.jp

Received 18 September 2014

Abstract
We studied the effectiveness of diamond nanoparticles (DNPs) dispersed in water as a lubricant additive between stainless steel plates and sintered tungsten carbide (WC) balls. DNP dispersions with concentrations of 0.01, 0.1 and 1 wt.% were prepared and used as lubricants under a load of 1.88 N, for 240,000 friction cycles. High-friction coefficients of more than 0.3 were observed in an initial period. Then friction coefficients declined and stabilised at values of approximately 0.1. The steady-state friction coefficients were independent of the DNP concentration and lower than that for distilled water. In the initial period, wear of both the plates and ball was obvious. In the steady-state period, additional wear on the plates was a little; however, ball wear scars were clearly observed. The size of the ball wear scars decreased with decreasing the DNP concentration. It is likely that DNPs were embedded mainly in the stainless steel plates, and the embedded DNPs protected the plates and wore the balls in the steady-state period. Compared with the lubrication under distilled water, the friction coefficient and wear of the plate under the lubrication by the 0.01 wt.% DNP dispersion were lower, and the wear of the ball by this lubrication condition was not higher.

Key words: Diamond nanoparticles, Water lubrication, Friction coefficient, Wear, Lubricant additive

1. Introduction
Reducing friction and wear is strongly demanded in mechanical systems, including metal working and mechanical devices, for long time. Although oils are most widely used as liquid lubricants, environmental problem happened in their leaks and disposals. Water is obviously environmentally friend liquid, and have been studied as liquid lubricants. Advantages of water used as liquid lubricants are high cooling capacity, good fire-resist, and low cost. However, there is a problem that viscosity of water is too low to make lubricant films between sliding surfaces. Many kinds of additives in water have been studied to improve the problem. Recently carbon nanomaterials such as fullerene, carbon nanotubes, and graphene (oxide) have been studied as the additives of water lubrications for their good tribological properties (Kinoshita et al., 2013; Liu et al., 2012; Song & Li, 2011).

These carbon nanomaterials above mentioned have graphite structures composed of sp² bonding. In carbon nanomaterials, only diamond nanoparticles (DNPs) have single crystal diamond structure composed of sp³ bonding, with a size of less than 10 nm. Diamond-structured materials such as diamond-like carbon (DLC) coatings are hard and their friction and wear are very low in water environment (Sutton, Limbert, Stewart, & Wood, 2013). DNPs are also expected to have good tribological properties under water lubrications. In addition, DNPs can be obtained with the production capacity in industrial scales by chemical vapor deposition or by detonating high explosive material (Galli, 2010; Holt, 2007). DNPs have showed good tribological properties as additives in oils (Chu et al., 2010; Shen et al., 2001). A tribological property of DNPs as additives in water is only studied under the lubrication between SiC and
silicon (Mori, Kanno, Nanao, Minami, & Ôsawa, 2008). It is necessary to study tribological properties of DNP additives under water lubrications between materials used in mechanical systems.

In this study, tribological properties of DNP dispersions in water were investigated using steel plates and tungsten carbide (WC) balls which are widely used in metal working, and the influence of DNP concentration in the dispersion was discussed. The lubricated surfaces on plates and balls were analysed by optical microscopy, contact surface profilometry and Raman spectroscopy.

2. Materials and methods

Commercial DNPs (Carbodeon uDiamond® Molto, Carbodeon NanoMaterial) were used in this study. This product is a DNP powder with crystal sizes of 4–6 nm that has a DNP content of more than 97%. Lubricant dispersions were prepared by adding DNP powder to distilled water and mixing for 5 min by ultrasonication. DNP dispersions with concentrations of 0.01 wt.%, 0.1 wt.% and 1 wt.% were prepared. Fig. 1 shows the as-prepared DNP dispersions. The test materials used in this study were lapped stainless steel (JIS-SUS304) plates and sintered tungsten carbide (WC) balls with a diameter of 2 mm. The surface roughness (arithmetic mean roughness, $R_a$) of the lapped plate surfaces was approximately 33 nm, and that of the ball surfaces was approximately 2 nm.

A tribometer with a reciprocating sliding configuration was used for the friction tests in this study. Friction tests were performed with a sliding width of approximately 2.5 mm, a sliding frequency of 600 rpm, duration of 240,000 cycles, under an applied normal load of 1.88 N. The average sliding speed was 40 mm/s, which implies that the sliding condition of lubrication regime is the boundary lubrication. Both the SUS304 plates and WC balls were pre-cleaned in ethanol, and then water for 5 min each using an ultrasonicator. The cleaned samples were placed in an acrylic box positioned on the sliding track of the tribometer. A sufficient amount of lubricant to cover the sliding area was added (approximately 2 ml). The acrylic box was covered and no water condensation observed inside the box’s wall during the 6-h friction experiment, which indicates no significant evaporation of the water. The lubricated surfaces of the plates and balls were investigated by optical microscopy, contact surface profilometry, and Raman spectroscopy. All of the plates and balls were carefully washed by ultrasonating in ethanol before analyses. Widths of plate wear tracks were determined by 3 times measurement average on each two different points. Widths of ball wear scars did by 3 times measurement average on one point.

Fig. 1  As-prepared DNP dispersions with concentrations of 0.01, 0.1 and 1 wt.% in comparison to distilled water.

3. Results and Discussion

Fig. 2 shows the change in friction coefficients for the distilled water and the DNP dispersions (concentrations 0.01, 0.1 and 1 wt.%) for 240,000 cycles. The friction coefficient measured under lubrication with distilled water was relatively constant at 0.4. The friction coefficients measured under lubrication by the DNP dispersions were initially high, and decreased to steady-state values. The lowest friction coefficient in the initial period was measured for the 0.01 wt.% DNP dispersion, and was approximately the same value as that of distilled water. Meanwhile, the friction...
coefficients for both the 0.1 wt.% and 1 wt.% DNP dispersions were initially greater than 0.5. The 1 wt.% DNP dispersion showed a sharp decline in friction from 0.5 to 0.12 after around 25,000 cycles. The 0.1 wt.% DNP dispersion also decreased to 0.12 after around 35,000 cycles. The 0.01 wt.% DNP dispersion required the longest time to reach a steady-state value of 0.12 after around 75,000 cycles.

Optical microscope images of wear on the plates and balls at 1,000, 10,000 and 100,000 cycles under lubrication by the 1 wt.% DNP dispersion are shown in Fig. 3. Wear was obvious on both the plate and ball surfaces. The plate wear surfaces had one feature. Moreover, the ball wear surfaces after 1,000 and 10,000 cycles (in the initial high-friction period) also appeared one feature. A central striation parallel to the sliding direction was observed on the ball wear scar that experienced 100,000 cycles (in the steady-state low friction period).
Fig. 4  Optical microscope images of the plate wear tracks under distilled water and the DNP dispersions with the different concentrations after 240,000 cycles of friction testing. 
(a) Distilled water, (b) 0.01 wt.% , (c) 0.1 wt.%, and (d) 1 wt.% DNP dispersions.

Fig. 5  Surface profiles of the same plate wear tracks shown in Fig. 4. 
(a) Distilled water, (b) 0.01 wt.% , (c) 0.1 wt.%, and (d) 1 wt.% DNP dispersions.
Fig. 6  Optical microscope images of the wear scars on WC balls after the tests in distilled water and the DNP dispersions with the different concentrations after 240,000 cycles. (a) Distilled water, (b) 0.01 wt.%, (c) 0.1 wt.%, and (d) 1 wt.% DNP dispersions.

Table 1 Widths of the plate wear tracks and ball wear scars for the 1 wt. % DNP dispersion lubricated system until 100,000 cycles, which were obtained from Figs. 3, 4(d), and 6(d).

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>138</td>
<td>139</td>
<td>137</td>
<td>127</td>
<td>128</td>
<td>127</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10,000</td>
<td>141</td>
<td>143</td>
<td>140</td>
<td>143</td>
<td>144</td>
<td>143</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100,000</td>
<td>145</td>
<td>148</td>
<td>142</td>
<td>370</td>
<td>371</td>
<td>368</td>
<td>119</td>
<td>120</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240,000</td>
<td>478</td>
<td>479</td>
<td>477</td>
<td>485</td>
<td>489</td>
<td>477</td>
<td>180</td>
<td>187</td>
<td>176</td>
<td>119</td>
<td>120</td>
<td>117</td>
</tr>
</tbody>
</table>

Table 2 Widths of the plate wear tracks and ball wear scars after 240,000 cycles with different lubrication conditions, which were obtained from Figs. 4, 5 and 6.

<table>
<thead>
<tr>
<th></th>
<th>Plate wear track (μm)</th>
<th>Groove width</th>
<th>Groove depth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Distilled water</td>
<td>280</td>
<td>284</td>
<td>275</td>
</tr>
<tr>
<td>0.01 wt.% DNP dispersion</td>
<td>250</td>
<td>253</td>
<td>249</td>
</tr>
<tr>
<td>0.1 wt.% DNP dispersion</td>
<td>312</td>
<td>313</td>
<td>311</td>
</tr>
<tr>
<td>1 wt.% DNP dispersion</td>
<td>478</td>
<td>479</td>
<td>477</td>
</tr>
</tbody>
</table>
Thus, under distilled water lubrication, wear was happened on areas of the full widths of the balls to each other. These full widths were also nearly close to the full widths (calculated in the surface profile of Fig.5) of plate wear tracks in the initial period (Fig.4). As mentioned above, the central striations grew mainly on the ball surface in the initial period. Parallel to the direction of sliding were also observed on the all ball wear scars. In contrast to the plates, the wear was obvious outside of the central striations on the ball surfaces.

Table 1 summarizes mean, maximum and minimum values of widths of the plate wear tracks and ball wear scars for the 1 wt. % DNP dispersion lubrications, which were obtained from Figs. 3, 4(d), and 6(d). After 1,000 and 10,000 cycles (in the initial high friction period), the plate wear tracks and ball wear scars had one feature. The full widths of the plate wear tracks and ball wear scars show similar values to each other. These full widths were also nearly close to the widths of the central striations on the wear tracks and scars after 100,000 and 240,000 cycles (in the steady-state period). These similar widths were shown by grey background in Table 1. Table 2 shows mean, maximum and minimum values of widths of the plate wear tracks and ball wear scars after 240,000 cycles with different lubrication conditions, which were summarized from Figs. 4, 5 and 6. Under distilled water lubrication, the width of the grooves of the plate wear track (calculated in the surface profile of Fig.5) corresponds to both the full widths of the plate wear track and the ball wear scar. Thus, under distilled water lubrication, wear was happened on areas of the full widths of both the plate wear track and ball wear scar. Under the lubrications by the DNP dispersions, the central striation widths of the plate wear tracks and ball wear scars showed nearly similar values to each other with the different DNP concentration. The widths and depths of the grooves for the DNP dispersions (calculated in the surface profile of Fig.5) were also nearly identical with the different DNP concentration. The widths of the grooves were nearly same to the widths of the central striations, not the full widths, of the plate wear tracks. These similar widths concerning about the central striations were shown by grey background in Table 2.

From these experimental results, we assumed a model of wear on the plate and ball surfaces in the initial and steady-state period shown in Fig. 7. The full widths of the plate wear tracks in the initial period were almost same to the widths of the central striations on the plate and ball surfaces in the steady-state period (Table 1). These results imply that the central striations would be formed only in the initial period and did not grow in the steady-state period (indicated red line of the contact area between the plate and ball in Fig. 7). The estimated initial contact is calculated to be 42 μm obtained from Hertzian contact theory and the measured central striations widths were more than 120 μm. This implies that the central striations were formed by wear. In the surface profiles in Figs. 5 (b)-(d), wear outside of the grooves (the central striations) was hardly recognized, which agree in that the wear outside of the central striations shown in Figs. 4 (b)-(d) was very little (indicated orange line of the contact area between the plate and ball in Fig. 7). The wear of the ball surfaces was obviously appeared (Figs. 6 (b)-(d)). As mentioned above, the central striations grew mainly in the initial period. Considering these facts, in the steady-state period, wear on the plates was very little and wear occurred mainly on the ball surfaces as shown in Fig 7. The assumption in the model shown in Fig. 7 that the central striations would be formed only in the initial period and wear would occur mainly on the ball surface in the steady-state period can explain the photos of the plate wear tracks and ball wear scars, and the surface profiles of the plate wear tracks.

Figure 7 Model of wear on plate and ball surfaces under DNP dispersion lubrications in the initial and steady-state periods.

Single-groove. Optical microscope images of the balls after 240,000 cycles were shown in Fig. 6. Central striations parallel to the direction of sliding were also observed on the all ball wear scars. In contrast to the plates, the wear was obvious outside of the central striations on the ball surfaces.
Raman spectra measured on the worn plate and ball surfaces are shown in Fig. 8. The Raman spectrum of the plate wear tracks lubricated by distilled water showed no carbon composite peak spectra. In contrast, the Raman spectra measured on the plate wear tracks under the lubrications by the DNP dispersions showed peaks at 1332 cm\(^{-1}\) and around 1600 cm\(^{-1}\), which correspond to first-order diamond Raman line and carbon components including sp\(^2\) bonds, respectively (Prawer et al., 2000). These peaks could also be measured in the as-received DNPs. This suggests that the DNPs were deposited on the plate wear tracks during the friction tests using the DNP dispersions. A peak at 1070 cm\(^{-1}\) was measured for all conditions used, including distilled water. On the ball wear scars lubricated by both distilled water and DNP dispersions, the Raman spectra showed no peaks between 1200 and 2000 cm\(^{-1}\). The peaks at 1070 cm\(^{-1}\) were observed that can be attributed to stretching and bending modes of carbonate in WC ball itself (Berger et al., 2014; Ma & Du, 2008; O’Donnell, Candarlioglu, Miller, Gentleman, & Stevens, 2010). It is summarized from the Raman spectra that DNPs existed in the steel plate surfaces and did not on the WC ball surfaces after the DNP dispersion lubrication.

From Table 1, the full widths of the ball wear scars by the DNP dispersions increased with the friction cycles. This means that the wear of the ball continuously occurred even in the steady-state period. In addition, from Table 2, the full widths of the ball wear scars under lubrication by the DNP dispersions increased with the DNP concentration. These results indicate that DNPs would wear the ball surfaces. The wear on the hard ball surfaces (Vickers hardness of WC is
greater than 1,000 HV) without DNPs was larger than that of the soft steel plate surfaces (Vickers hardness of SUS304 is 129 HV) with DNPs. It is reported that DNPs dispersed in oil was tightly embedded to contact steel surfaces and increase wear resistance of the steels (Chou & Lee, 2010; Puzyr, Burov, Selyutin, Voroshilov, & Bondar, 2012). Thus, also in this study, it is expected that DNPs were embedded on the plate surfaces due to the lubrication and that the embedded DNPs protected the steel surfaces. The low friction coefficients that were achieved in the steady-state period would arise from the interaction between these hard surfaces of the embedded DNPs and the WC balls.

DNPs would provide not only protective effect but also abrasive wear. As shown in Fig.2, with increasing the DNP concentration, the initial friction coefficients became higher and the number of initial cycles having the high friction decreased. In the initial period, the plate surface would not have enough amounts of the embedded DNPs to protect itself, and DNPs would wear the plate surface. It is expected that the higher concentration of DNP increased the rates of both abrasive wear and embedding. The higher rate of the abrasive wear increased the friction coefficients, and the higher rate of the embedding reduced the number of cycles to reach a steady-state friction.

The friction coefficients after reaching steady-state frictions under the lubrications by the DNP dispersions were lower than that using distilled water. The wear of the plates lubricated by the DNP dispersions, which was occurred on almost all the central striations in the initial stage, was lower than that under the lubrication by distilled water. Especially the depths of all the plate wear tracks lubricated by the DNP dispersions were much lower than that lubricated by distilled water. The shape in the ball wear scar lubricated by distilled water was oval, arising from the deep depth of the plate wear track. In contrast, for the lubrications by the DNP dispersions, the relative flat plate wear track resulted in the circular shape of the ball wear scars. Thus, it is difficult to compare wear volumes of the ball wear scars. The diameters of the ball wear scars lubricated by the DNP dispersions decreased with decreasing the DNP concentration. The 0.01 wt% DNP dispersions provided the smallest diameter of the ball wear scars in this study, which was little smaller than the width of the ball wear scar under the lubrication by distilled water. However, since the embedded DNP on the plate wear tracks would provide the abrasive wear of the ball surfaces, it is difficult to say the advantage of the DNP dispersions for the ball wear. We concluded that the optimum DNP concentration to reduce friction and wear of the plate and to provide not high wear of the ball was around the 0.01 wt%.

4. Conclusions

In this study, the tribological properties of the DNP dispersions in water with the different DNP concentrations were investigated using the steel plates and WC balls. Initially, the lubricated systems showed high friction, which declined and stabilized after the number of cycles. In the initial period, DNPs would wear both the plate and ball surfaces, forming the central striations. At the same time, DNPs were also embedded on the stainless steel plate surface. The steady-state period would be reached when the amount of the embedded DNPs became sufficiency to protect the plate surface. The high concentration of DNPs resulted in the higher friction and shorter cycles of the initial period. In the steady-state period, it is thought that the embedded DNPs directly contacted the hard WC ball surfaces, which resulted in the low friction and low plate wear, and high ball wear. Compared with the lubrication under distilled water, the lubrication by the 0.01 wt.% DNP dispersion provided the lower friction coefficient and wear of the plate, and the not higher wear of the ball.

Acknowledgements

This research was partially supported in the Science Students Encourage Research Funding, Graduate School of Science and Technology, Okayama University and Grants in aid for Scientific Research (B) (26289028).

References


