Tribological Properties of High Hardness ta-CNx Coatings Deposited by Filtered Arc Deposition with Block-on-Ring Tribotester

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Abstract
Low friction and high wear resistance are strongly needed desired in boundary lubrication condition for industrial usage. Carbon nitride (CNx) coating is one of the promising materials, but the hardness of conventional CNx coating was only 10 GPa of nanoindentation hardness. In order to coat high hardness ta-CNx, we developed a dynamic mixing deposition method combining the filtered arc deposition system and nitrogen ion beam source. Nitrogen content was controlled by the nitrogen partial pressure in the deposition. Nanoindentation result gave the hardness of ta-CNx from 75 to 70 GPa, under the nitrogen content from 5 to 8 at.%. In order to clarify the tribological performance of ta-CNx coatings under the boundary lubrication, block on ring friction test was carried out. As a result, this new ta-CNx showed much higher wear resistance compared to the former soft CNx and hard ta-C coatings under PAO lubrication for the block-on-ring tribotester.

Keywords: ta-C, ta-CNx, filtered arc deposition, friction, wear

1 Introduction

There are many researches which focus on the use of Diamond-like Carbon (DLC) coatings under boundary lubricated contacts to reduce the friction loss and to protect the mechanical components (Grill, 1999, Vengudusamy et al., 2012). Carbon nitride (CNx) coating is an unique low friction material, which realizes ultra-low friction coefficient of 0.01 in nitrogen atmosphere (Umehara et al., 1998, Umehara et al., 2000, Tokoroyama et al., 2000). It was reported that Si₃N₄/CNx or CNx/CNx provided friction coefficients of 0.01-0.001 in dry nitrogen gas (Adachi et al., 2005) and in water (Zhou et al., 2007). Also the influence of UV irradiation in low frictional performance of CNx coatings was shown (Tokoroyama et al., 2012) and it is expected to be applied on sliding parts of machines.
However, there is a problem of CNx coatings that hardness is relatively low. In normal coating methods, the hardness of CNx is lower than that of DLC coatings. For example, the hardness of CNx shows 3.9-21.6 GPa by Chemical vapor deposition (CVD) [9], 4-17Pa by magnetron sputtering (MS) and 10-20 GPa when deposited by Ion Beam Assisted Electric Beam Deposition (IBA-EBD) (Tokoroyama et al., 2011). Doping a-C films with nitrogen has the added advantage due to reduction of residual stress in coatings, but decreased the hardness (Hammer et al., 1997).

Therefore, it is necessary to improve the mechanical properties of CNx to increase the durability of CNx coatings. Based on this motivation, doping nitrogen into tetrahedral amorphous carbon (ta-C) was considered in this study. It is known that ta-C is made from ion or plasma beams with a high ion fraction and a narrowly defined ion energy. Filtered Arc Deposition (FAD) is widely used for ta-C deposition because it can supply high fraction carbon ions with certain energy (Takikawa et al., 2003). Their ta-C showed more than 70 GPa in hardness.

Therefore, we proposed a new deposition method for ta-CNₓ with Nitrogen ion beam assisted filtered arc deposition to deposit hard ta-CNₓ. Also we investigated the effect of nitrogen on the mechanical properties, the crystal structures, and tribological properties with block-on ring friction tester in oil lubrication by changing the nitrogen content in the CNx coating systematically.

2 Experimental

For the deposition of high hardness tetrahedral amorphous carbon nitride (ta-CNₓ) coatings, we developed the dynamic mixing deposition method combining the filtered arc deposition system and nitrogen ion beam system (Ion Beam Assisted Filtered Arc Deposition, IBA-FAD) as shown in Fig.1. Carbon ions from a cathodic arc evaporation and nitrogen ions which were provided by ion source were simultaneously deposited on the substrate. Nitrogen content in the ta-CNₓ coatings was controlled by nitrogen partial pressure from $5.2 \times 10^{-2}$ to $3.94 \times 10^{-1}$ Pa. Nitrogen content in ta-CNₓ was measured by XPS. For the measurement of hardness of the coatings, nanoindenter was used. To clarify the effect of nitrogen adding on bonding structure of ta-CNₓ coatings, Raman spectroscopy was used. Thickness of ta-C was measured by the measurement of step height of coating after masking method with AFM.

In order to clarify the tribological performance of ta-CNₓ coatings under the boundary oil lubrication, block on ring friction test was carried out. AISI440C block specimen was coated with ta-CNₓ coatings which were deposited in the same batch. Figure 2 shows the schematics of block-on-ring friction tester. Normal load was applied by a dead weight system. Friction force was measured by strain gauges system. The part of SAE4620 ring specimen was dipped in oil bath. Sliding conditions are shown in Table 2. The lubricating oil used in the test was a base oil poly alpha olefin (PAO) and oil temperature was set to be room temperature.
Fig. 1 Schematics of deposition apparatus of filtered arc deposition assisted with Nitrogen ion irradiation (Ion beam assisted filtered arc deposition, IBAFAD)

### Table 1 Parameters of ta-CNx deposition by using IBAFAD

<table>
<thead>
<tr>
<th>Ar and N ion bombardment</th>
<th>Ar and N flow rate/sccm</th>
<th>8 and 5</th>
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<tr>
<td>Pressure/Pa</td>
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<td>Bias/V</td>
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<table>
<thead>
<tr>
<th>Carbon source</th>
<th>Arc current/A</th>
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<tbody>
<tr>
<td></td>
<td>Bias/V</td>
<td>-100</td>
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<table>
<thead>
<tr>
<th>Coating deposition</th>
<th>Partial pressure/Pa</th>
<th>0, 0.05, 0.17, 0.30, 0.39</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen source</td>
<td>Acceleration</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Bias/V</td>
<td>-100</td>
</tr>
</tbody>
</table>
3 Results and discussion

3.1 Material properties of ta-CNx

In order to check the effect of Nitrogen content on material properties of ta-CNx, we have deposited various ta-CNx under different Nitrogen partial pressure in the process chamber.

Figure 3 shows the effect of partial pressure of Nitrogen in the process chamber on Nitrogen content in ta-CNx coatings. We evaluated the Nitrogen content in ta-CNx by the XPS analysis. It can be seen that Nitrogen content in ta-CNx can be controlled by the changing of the partial pressure of Nitrogen in the chamber. Maximum Nitrogen content was 8.1 at%. However the Nitrogen content was saturated with the increasing of Nitrogen partial pressure. In order to know the reason why Nitrogen contents were not proportional to Nitrogen partial pressure, current density of ion was measured by Faraday
cup which was located 500 mm away from the exit of ion beam generator. Figure 4 shows the relation between the current density and nitrogen partial pressure. Taking it by and large, ion current density decreased with the nitrogen partial pressure. According to Paschen's law, the breakdown voltage (voltage necessary to discharge) across the gap was reduced and then increased gradually as the pressure.

\[ V = \frac{BPD}{\ln(4PD) - \ln\left(\ln(1 + \frac{1}{\gamma_{se}})\right)} \]  

(1)

Where \( V \) is the breakdown voltage, \( P \) is the pressure, \( d \) is the gap distance, \( \gamma_{se} \) is the secondary electron emission coefficient, \( A \) is the saturation ionization in the gas, and \( B \) is related to the excitation and ionization energies. The constants \( A \) and \( B \) are determined experimentally. Normally, the lower the breakdown voltage the higher ionization rate and current. Thus the results in Fig. 4 indicate that the nitrogen partial pressure in this study belongs to monotonic increase region of Paschen’s Law. Consequently, it is difficult to raise the nitrogen content by increasing nitrogen partial pressure during this deposition process.

Figure 5 shows the effect of Nitrogen content in the process chamber on ID/IG ratio in Raman spectroscopy of ta-CNx. It can be seen that ID/IG ratio was increased with the increasing of Nitrogen content. Also we observed the reduction of FWMH of G peak with increasing of Nitrogen contents. So it can be considered that volumetric fraction of graphite-like structure was increased with the Nitrogen content.

Figure 6 shows the effect of Nitrogen content in the process chamber on hardness of ta-CNx. It can be seen that hardness was decreased with the increasing of Nitrogen content. It is important that we obtained very hard ta-CNx coating that contains about 8 at% of Nitrogen. Even if the Nitrogen contains 8 at%, the hardness of ta-CNx was about 60 GPa. When we coated CNx by Nitrogen ion beam assisted deposition IBAD that has done by Carbon vaporizing deposition and Nitrogen ion irradiation simultaneously. By using the IBAD method, the hardness of CNx was about 20 GPa. So now we obtained much harder CNx by this method than that by IBAD by 3 times.

Fig.3 Effect of partial pressure of Nitrogen in the process chamber on Nitrogen content in ta-CNx coatings
Fig. 4 Relationship between the current density and nitrogen partial pressure.

![Graph showing the relationship between current density and nitrogen partial pressure.]

Fig. 5 Raman spectroscopy of ta-CNx which thickness is 0.32 μm, bias voltage for substrate is 500 V and Nitrogen partial pressure is 0.3 Pa.

![Raman spectroscopy graph showing normalized intensity against Raman shift.]

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3.2 Friction and wear properties of ta-CNx coated block sliding against steel ring in PAO oil

Figure 8 shows friction coefficient of former IBAD CNx and this FAD ta-CNx in oil lubrication as a function of number of cycles. The former IBAD CNx has 10 GPa hardness and 0.1 μm thickness. This FAD ta-CNx has 60 GPa hardness and 0.3 μm thickness. In the case of former IBAD CNx, friction coefficient increase rapidly under this severe sliding condition and reached to 0.1. On the other hand, this FAD ta-CNx has kept low friction as 0.0035 of friction coefficient as shown in Fig.8.

Figure 9 shows the comparison of friction coefficient between ta-C and this FAD ta-CNx in oil lubrication under incremental step-up normal loads from 98 N to 294 N. It can be seen that ta-CNx
shows lower friction coefficient that ta-C in 80 °C PAO. The ta-C has 80 GPa hardness and 1 μm thickness. This ta-CNx has 60 GPa hardness and 0.3 μm thickness.

Figures 10 and 11 show optical images of wear scars of ta-CNx and ta-C coated blocks after sliding test of Fig.9, respectively. It can be seen from Fig.11 that ta-C showed severe wear that shows partially total removal of coating. On the other hand, ta-CNx did not show severe wear as shown in Fig.10. By the measurement of wear depth with a stylus profilometer, ta-C showed 0.46 μm of wear depth and ta-CNx showed less than 0.01 μm of wear depth for the specimen as shown in Figs. 10 and 11. This result is slightly strange because softer ta-CNx showed more wear resistance than ta-C. On the basis of the observation of wear scar, it can be considered that low brittleness of ta-C caused larger wear amount than ta-CNx. So we need to clarify the specific deformation and fracture properties of ta-CNx.
4 Conclusions

In order to improve wear resistance of CNx, we proposed new deposition method of ta-CNx as Nitrogen ion beam assisted filtered arc deposition (IBA-FAD). After the deposition of ta-CNx on the AISI 440C block specimen, we investigate the materials, friction and wear properties. Obtained main results are following:

As the nitrogen content in the ta-CNx coatings increased, the hardness of the coatings decreased. Also, Raman result provided the increase of ID/IG ratio and the decrease of G peak FWHM with the increase of nitrogen content. From those results, it can be considered that sp² content and/or sp² cluster size in the ta-CNx coatings increased as the nitrogen content increased. From the block-on ring tests, developed ta-CNx with IBA-FAD showed more stable friction properties than former IBAD CNx. Also, developed ta-CNx showed lower friction coefficient and high wear resistance than the former IBAD CNx. It can be consider that these stable friction properties and wear resistance depend on high hardness of developed ta-CNx.
References


