Characteristics and Applications of DLC films

1. Introduction

NTN Group strives to reduce its environmental footprint and thus remains committed to continued mitigation of environmental impacts caused by its corporate activities through improving energy efficiency and utilization of resources in its production activities. As an example, bearing engineers have been proposing reduced use of rare materials, such as Mo, included in bearing lubricant, as well as reduction in the amount and viscosity of the lubricating oil used which, result in lower bearing torque. However, these attempts can result in deteriorated lubrication of the bearing components, and conventional techniques may fail to sufficiently lubricate the bearing components involved.

Surface modification appears to be a promising technique that can dramatically improve the tribological characteristics of bearing components. Bearing engineers have been considering the adoption of various hard films in order to alleviate friction and wear on sliding surfaces within bearings. In particular, Diamond-Like Carbon (DLC) film boasts higher hardness, excellent wear resistance, and lower friction coefficient and has been applied to automotive parts, dies, and tools.

There are various reports available about applications of DLC films: examples state that when sliding in nitrogen gas or a vacuum, a-C:H (hydrogenated amorphous carbon), which is a hydrogen-rich DLC, exhibits an extremely low friction coefficient of 0.001\(^1,2\); another report says that ta-C (tetrahedral amorphous carbon), which is a hydrogen-free DLC, exhibits low friction when lubricated with oil in an automotive gasoline engine\(^3\). A variety of DLC films are available, and their sliding properties can vary significantly depending on coating method and/or conditions and the operating environment. Therefore, the optimal DLC film design must be selected based on the expected operating conditions. The following article describes various properties of DLC films and examples of their application to molding dies.

2. Features of DLC films

2.1 What is DLC film?

A DLC film can be defined as an amorphous film (Fig. 3) consisting of an irregular mixture of diamond atoms that form sp\(^3\) bonds (diamond structure shown in Fig. 1) and diamond atoms that form sp\(^2\) bonds (graphite structure shown in Fig. 2). To provide a concept diagram that helps to better explain DLC films, Frrai and Robertson\(^4\) have proposed a ternary phase diagram such as given in Fig. 4. In this diagram, the corner at the top represents diamond, the lower left corner graphite, and the lower right corner hydrogen.

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From the view point of environmental and energy issues, vigorous efforts have been put into research and development activities for tribological coating films in order to reduce friction and wear of sliding surfaces. In particular, diamond-like carbon (DLC) coatings have superior low-friction and anti-wear properties compared to other coating films, and they are attracting a great amount of attention from tribology researchers and engineers. The friction and wear properties of DLC films, however, depend on their use conditions as well as their production processes, and therefore it is necessary to choose appropriate DLC films according to their use conditions and engineering purposes. This article introduces various properties of DLC films.

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Table 1 summarizes the general physical properties of carbon materials including graphite, diamond, and DLC films. Data for Young’s modulus, hardness number, and the electrical characteristics of DLC film are similar to those of diamond, and the thermal conductivity of DLC film is similar to that of graphite. The variation in physical property values of DLC films exist due to variation in proportion of sp3 bonds to sp2 bonds and hydrogen content.

Table 1 Comparison of characteristics of carbon material

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Graphite</th>
<th>Diamond</th>
<th>DLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.25</td>
<td>3.52</td>
<td>1.0~3.0</td>
</tr>
<tr>
<td>Specific electric resistance</td>
<td>$10^{-3}$</td>
<td>$10^{15}$~$10^{16}$</td>
<td>$10^{8}$~$10^{14}$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.4~2.1</td>
<td>1000~2000</td>
<td>0.2~30</td>
</tr>
</tbody>
</table>
| Lattice constant (nm)         | a=0.2456 | c=0.6708 (interlayer) | ... | ...
| Young’s modulus (GPa)         | ...      | 1000~2000 | 100~800      |
| Hardness number (Hv)          | ...      | 10000~12000 | 1000~8000   |
| Oxidation start temperature   | 400~450  | 600     | 300~500      |

2.2 Coating methods for forming DLC films

DLC films can be created from solid carbon or hydrocarbon gases such as methane, acetylene and benzene and are usually formed in a vacuum chamber. Depending on the carbon source used, the DLC film falls within one of the following two categories:

(1) PVD: Physical Vapor Deposition

A process that uses solid carbon as a starting material, wherein solid carbon is evaporated and then the resultant carbon vapor is allowed to deposit on a substrate to form the DLC film.

(2) CVD: Chemical Vapor Deposition

A process that uses hydrocarbon gas as a starting material, wherein the gas is decomposed in a vacuum chamber and then the resultant carbon vapor is allowed to deposit on a substrate to form the DLC film.

By using solid carbon as an evaporation source, the PVD process can produce a DLC film solely composed of carbon. In contrast, since the CVD process uses hydrocarbon gas as a starting material, the resultant DLC film unavoidably contains hydrogen atoms of approximately 15 to 50 atm%. Either the PVD or CVD processes can be applied in various methods. Fig. 5 summarizes typical coating processes applied to form DLC films.
Table 2 lists several general physical characteristics of DLC films formed by various coating processes. It has been known that characteristics of synthesized DLC films can vary greatly depending on starting materials, atomic elements added, and coating conditions. The UBMS (Unbalanced Magnetron Sputtering) process listed in Table 2 is one type of sputtering process, and is characterized by an unbalanced magnetic field that is employed to expand a plasma layer in the vicinity of the substrate. Because the plasma density near the substrate is increased, the ion assist effect (ions are allowed to collide the substrate) is enhanced; consequently, the film characteristics including density and adhesion are improved.

The AIP (Arc Ion Plating) process uses a solid carbon cathode and the chamber inner wall as an anode in order to trigger an arc discharge and allow carbon on the target surface to evaporate. The resultant carbon vapor is ionized and is allowed to deposit on the sample surface to which a negative bias voltage is applied. As a result, a DLC film with a higher degree of adhesion is formed.

In a plasma CVD process, hydrocarbon gas (such as methane, acetylene, benzene, etc.) is decomposed in a vacuum chamber to generate hydrocarbon ions that are accelerated and allowed to collide into a substrate to which negative voltage is applied resulting in the DLC film. Because of using gas as a starting material, the CVD process features better “coverage” and is suitable for forming a DLC film on samples with complex geometry. Also, with this process, a DLC film of uniform thickness can be formed without the need to reorient the sample.

2.3 Comparison of DLC films with various other hard coatings
2.3.1 Characteristics in general
Table 3 summarizes the characteristics of DLC films and other hard coatings. DLC films boast particularly high hardness and excel in anti-seizure quality. However, DLC films have an unavoidable drawback that is, poor adhesion to a substrate. Poor adhesion occurs because stresses within a DLC film are high, and carbon atoms, which are chemically stable, do not readily coagulate with a dissimilar material. Therefore, improved DLC film adhesion poses an engineering challenge.

2.3.2 Friction wear resistance
Using the NTN Savin type wear test rig, NTN has evaluated the sliding characteristics of DLC films (formed with UBMS process) and of various other nitride coatings.

This test rig is designed to maintain sliding contact between the flat test piece and a driven rotating cylinder which is crowned. Fig. 6 illustrates the configuration of the NTN Savin test rig, and Table 4 summarizes the test conditions applied. The test rig uses a crowned cylinder so that uneven contact does not occur between the test piece and cylinder, thus achieving a much more accurate assessment of the film’s wear resistance. Fig. 7 summarizes the test results, where the specific wear has been calculated based on the width of wear marks found on the test piece and the friction coefficients that have been determined based on friction values measured with the load cell.

The specific wear of DLC film is 1/6 or less compared with that of TiN, which was the best of the nitride films tested. In addition, the friction coefficient of DLC film is about 0.2 while the friction coefficients of other hard films fall in a range of 0.4 to 0.8, indicating the DLC film features excellent friction characteristics.
Thus, the DLC film appears to be a promising means for creating a highly wear-resistant surface treatment used on machine parts/components, dies, and tools.

### Table 3: Characteristics of DLC films and other hard coatings

<table>
<thead>
<tr>
<th>Film type</th>
<th>Color</th>
<th>Hardness number (HV)</th>
<th>Corrosion resistance</th>
<th>Oxidation resistance</th>
<th>Seizure resistance</th>
<th>Adhesion</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC</td>
<td>Gray to black</td>
<td>1000−8000</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>△</td>
<td>Cutting tools, dies, functional films</td>
</tr>
<tr>
<td>TiN</td>
<td>Gold</td>
<td>2000−2400</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>Cutting tools, dies, jewelry</td>
</tr>
<tr>
<td>ZrN</td>
<td>White gold</td>
<td>2000−2200</td>
<td>□</td>
<td>△</td>
<td>□</td>
<td>□</td>
<td>Jewelry</td>
</tr>
<tr>
<td>CrN</td>
<td>Silver white</td>
<td>2000−2200</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>Machine parts/components, dies</td>
</tr>
<tr>
<td>TiC</td>
<td>Silver white</td>
<td>3200−3800</td>
<td>△</td>
<td>△</td>
<td>□</td>
<td>□</td>
<td>Cutting tools, dies</td>
</tr>
<tr>
<td>TiCN</td>
<td>Purple to gray</td>
<td>3000−3500</td>
<td>△</td>
<td>△</td>
<td>□</td>
<td>□</td>
<td>Cutting tools, dies</td>
</tr>
<tr>
<td>TiAlN</td>
<td>Purple to black</td>
<td>2300−2500</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>□</td>
<td>Cutting tools, dies, jewelry</td>
</tr>
</tbody>
</table>

### Table 4: Test conditions

<table>
<thead>
<tr>
<th>Test piece</th>
<th>Coating method</th>
<th>Hardness, Gpa</th>
<th>Thickness, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>UBMS</td>
<td>26</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>AIP</td>
<td>53</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>CVD</td>
<td>15</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 3. Coating method-dependent variation in characteristics of DLC films

#### 3.1 Sliding wear characteristics

Fig. 8 plots the NTN Savin type wear test results of three DLC film samples, wherein the DLC films of these samples were prepared by UBMS process, AIP process, and plasma CVD process previously described in Sec. 2.2. Table 5 summarizes the coating methods, hardness numbers and thicknesses of these samples. The test conditions are the same as those specified in Sec. 2.3.2 except in that the test duration was changed to 30 minutes.

It is apparent that among three DLC film types, the UBMS process boasts best wear resistance and the AIP process features the lowest friction coefficient.

![Fig. 6 Wear test rig](image)

![Fig. 7 Wear property and coefficient of friction of each specimen specimens](image)

![Fig. 8 Wear property and coefficient of friction of each specimen](image)
3.2 Power of adhesion to substrate

NTN performed an adhesion evaluation test per the Rockwell indentation test method to determine adhesion of the DLC films which were tested in Sec. 3.1 to substrates. The Rockwell indentation test forces a cylindrical diamond indenter into each DLC film sample under a particular load (1,470 N) to form an indentation mark on the film. The quality of adhesion of the DLC film to a substrate has been evaluated based on the evidence of cracking or flaking of the film around the indentation mark. Figs. 9 through 11 show the resulting test samples.

In this evaluation, DLC film (A) has not developed cracking or flaking; DLC film (B) has developed radial cracks, though not flaking; DLC film (C) has exhibited severe flaking around the indentation.

Generally, DLC films are prone to peeling because their hardness is very high and internal stress exists: therefore realization of reliable adhesion to a substrate poses an engineering challenge. Techniques for improving film-to-substrate adhesion include:

- Higher substrate hardness (created by nitriding, shot peening, etc.)
- Surface pre-treatment (by chemical etching, abrasive blasting, etc.)
- Adoption of an intermediate layer that is highly affinitive to both the substrate and DLC film

Through adoption of techniques best suited for the intended operating conditions, a DLC film will positively adhere to a substrate.

As described above, DLC films can have diverse characteristics depending on coating method and conditions adopted. The optimal coating method and conditions for forming a DLC film need to be selected according to the intended application and performance requirements.

4. Applications to dies-DLC film application to dies for sintered metal moldings

In molding/forming work for sintered copper alloy parts, tungsten carbide dies are usually used because of their excellent wear resistance. However, in this type of work, excessive wear is occasionally observed on the dies even though the tungsten carbine material boasts significantly higher hardness compared with the copper alloy material. As a result, dies of much longer life have been increasingly needed. To address this challenge, NTN has attempted to adopt DLC films that provide much greater wear resistance.

Using the NTN Savin type wear test rig, NTN has evaluated wear resistance of non-coated tungsten carbide test pieces and tungsten carbide test pieces coated with a DLC film. The DLC film used was formed using the UBMS method. Table 6 summarizes the test conditions applied; Figs. 12 and 13 show wear marks found on the sliding surfaces; and Figs. 14 and 15 plot the resultant profile measurements on the worn surfaces of the test pieces.

The tungsten carbide-only test piece has exhibited a noticeable wear mark on its sliding surface even though it has undergone sliding contact with a sintered copper alloy member (a relatively soft material). The maximum depth of wear has reached 0.8 mm. In contrast, the test piece consisting of tungsten carbide

| Test piece | Tungsten carbide (WC-Co), OD 48 mm, thickness 7 mm, surface roughness 0.005 mmRa |
| Mating material | Sintered copper alloy (Cu58%, Fe40%), surface roughness 0.3 mmRa |
| Load | 50 N |
| Speed | 0.1 m/s |
| Time | 30 min (sliding distance 180 m) |
| Environment | Under blowing of dry air, temperature 0–20%RH |
coated with DLC film exhibited a wear depth of 0.04 µm which is 1/20 that of the uncoated test piece. The DLC film has helped dramatically reduce wear on the tungsten carbide test piece.

The reason tungsten carbide (WC-Co) wears as a result of sliding against the softer sintered copper alloy may be because the copper atoms diffuse into the cobalt particles at the contact interface. The cobalt particles act as a binder in the tungsten carbide structure. As a result of this diffusion, the Cu concentration between the WC and Co particles increases, thereby deterioration the mechanical strength of the tungsten carbide structure. By coating the surface of a tungsten carbide die with a DLC film, which does not readily react with copper atoms while maintaining wear resistance, wear on the die is much reduced. In addition, based on endurance test results with a die used commercially for sintered copper alloy, it has been verified that the life of the die coated with the DLC film is much longer compared with a non-coated die of a same geometry.

5. Conclusion

As described above, the DLC film treatment is a technique that is effective in extending life of dies and tools. Boasting a higher degree of wear resistance and lower friction, the DLC coating provides a promising technology that helps address environmental and energy issues. NTN will attempt to further develop this technology and expand the scope of its applications.

References
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2) J. Andersson et al., Wear, 254 (2003), 1070-1075
3) M. Kano et al.: Proceedings of The Third Asia International Conference on Tribology, October 2006, Kanazawa, 399