Novel Diamond-Like Carbon Film "HC-DLC" for Engine Parts That Slide on Soft Metals

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We have developed a new diamond-like carbon film "HC-DLC," which is produced by vacuum arc deposition and contains hydrogen. With its appropriate hydrogen content, this film obtained extremely low attackability to soft metals without compensating its high wear resistance and seizure resistance in engine oil containing MoDTC. The film demonstrates excellent performance in protecting piston pins that repeatedly slide on soft metals. To meet market needs, the mass production of the film started in the fall of 2019, and now further application to the next-generation high-efficiency engines is under consideration.

Keywords: DLC, MoDTC, piston pin, vehicle engine parts, sliding

1. Introduction

Although vehicles will be electrified rapidly in the future, the majority of them will be equipped with a combination of an engine and motor, even in the 2050s. Therefore, the number of engine-mounted vehicles will continue to increase. The load exerted on engine piston pins is increasing, as the engine is downsized and its efficiency is improved. Consequently, higher seizure resistance and wear resistance are required of them.

As the currently effective method of improving the seizure resistance and wear resistance of piston pins, the method involves coating the piston pins with a diamond-like carbon (DLC)*[1] film. It is known that the hydrogen-containing DLC films used for coating piston pins react with molybdenum dithio-carbamate (MoDTC)*[2], an engine oil additive, and cause abnormal wear of the pins.(1)

Conversely, hydrogen-free high hardness DLC films produced by the vacuum arc vapor deposition method or other suitable method protect the piston pins from abnormal wear, even when these pins are used in engine oil containing MoDTC. However, hydrogen-free DLC films are disadvantageous in that they demonstrate high attackability to the mating material and therefore are unsuitable for sliding with soft metal parts, such as piston pins.

To overcome the above situation, the authors developed a new DLC film called "HC-DLC." The new film does not suffer abnormal wear, even in engine oil containing MoDTC and demonstrates low attackability to soft metals.

2. Outline of HC-DLC Film

A DLC film is an amorphous thin film containing carbon as a major component, and it comprises a diamond structure (sp^3 structure) and graphite structure (sp^2 structure). The features of the new film can be controlled by changing the sp^3 structure/sp^2 structure ratio and the ratio of hydrogen taken into the structures. As a conceptual diagram of a DLC film based on these ratios, A. C. Ferrari and J. Robertson proposed the following ternary phase diagram (Fig. 1).(2)

Among DLC films containing hydrogen, a-C:H*[3] films are used for piston pins and many other parts. This type of films are mainly produced by the plasma chemical vapor deposition (CVD)*[4] method or sputtering method.

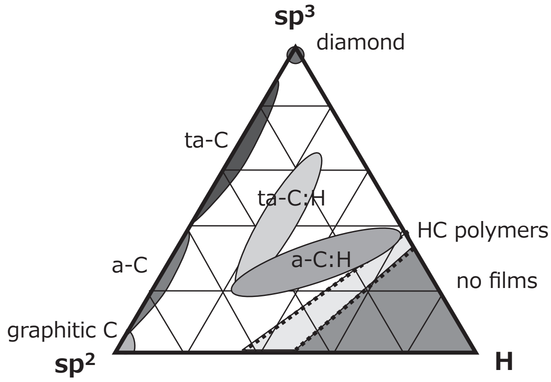

Fig. 1. Ternary phase diagram of DLC

Among hydrogen-free DLC films, ta-C*[5] films produced by the vacuum arc vapor deposition method are mainly used. When a-C:H films and ta-C films are compared, both of them are excellent in slidability, but ta-C films containing a lot of sp^3 structure exhibit higher hardness and heat resistance. Meanwhile, a-C:H films are known to react with MoDTC, which is often used as a friction modifier for engine oil, causing abnormal wear. Therefore, depending on applications, a-C:H films are unsuitable for piston pins. Conversely, ta-C films contain many hard particles called droplets in the production process. Although these particles are removed in the lapping process after film formation, they cannot be completely removed. Depending on the usage environment, the particles raise a problem of peering off the ta-C films and damaging the films themselves and mating sliding members.

Due to their high attackability to the mating material, ta-C films are unsuitable for piston pins that slide on aluminum (Al), copper (Cu), or other soft metal. In addition, MoDTC is often added to engine oil to further reduce the fuel consumption of vehicles, and this makes using a-C:H films for piston pins difficult.

The HC-DLC we developed is a ta-C:H*[6] film containing hydrogen. When the film is produced by the vacuum arc vapor deposition method, a hydrocarbon gas is introduced into the film formation atmosphere to take hydrogen into the film. The DLC film exhibits a structure between the ta-C film structure and a-C:H film structure. As a result of structural optimization, we succeeded in developing a new DLC film exhibiting excellent characteristics required for piston pins. In particular, the new DLC film eliminates abnormal wear, even in engine oil containing MoDTC, and it exhibits low attackability to Al, Cu, and other soft metals.

3. Performance Evaluation of HC-DLC Film

3-1 Properties of DLC

The properties of HC-DLC and conventional DLC are compared in Table 1.

HC-DLC and ta-C films are produced on the same film-forming equipment. In their production process, a hydrocarbon gas is introduced to take hydrogen into the films. In the test for determining the properties of the above films, the test samples were prepared under the same condition for the adhesion layer with base material, to compare the difference in the DLC film only. Additionally, since the DLC film produced by the vacuum arc vapor deposition method increased surface roughness due to the droplets, the HC-DLC and ta-C film samples were lapped under the same condition after formation of the films.

Table 1. Property comparison between HC-DLC and conventional DLC

	HC-DLC (ta-C:H)	ta-C	a-C:H
Production method	Vacuum arc vapor deposition method		Plasma CVD method
Raw material	Graphite Hydrocarbon gas	Graphite	Hydrocarbon gas
Film thickness	1 μm	1 μm	3 μm
Hydrogen content	13 at%	-	26 at%
Hardness	39 GPa	56 GPa	23 GPa

3-2 Wear resistance of HC-DLC Film

To check whether the addition of MoDTC causes abnormal wear of the HC-DLC film, we carried out a ball-on-disk test (Fig. 2 and Table 2) for engine oils with and without MoDTC, and the test results are shown in Fig. 3.

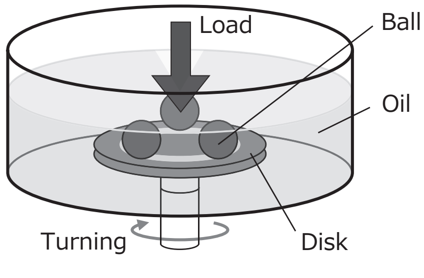

Fig. 2. Outline of ball-on-disk test

Table 2. Ball-on-disk test conditions

Disk	SCM415 (DLC-coated)
Ball	SUJ-2, φ3/8 inch, fixed
Load	250 N
Turning	1500 rpm, φ15 mm
Oil	Engine oil (5W-30), 80°C, Presence or absence of MoDTC
Time	40 min

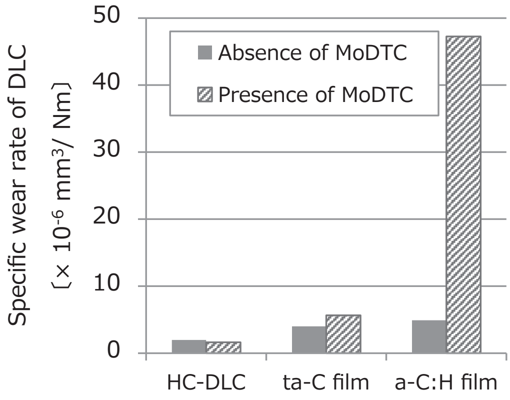

Fig. 3. Ball-on-disk test results

The HC-DLC and ta-C films were worn at almost the same rate, irrespective of the presence or absence of MoDTC, while the a-C:H film was significantly worn when MoDTC was added. The above results verified that HC-DLC does not suffer abnormal wear, even in a sliding environment where an a-C:H film is worn abnormally.

3-3 Attackability of HC-DLC film to mating material

A cylinder-on-disk test (Fig. 4 and Table 3) was carried out to check the attackability of HC-DLC to soft metals. The test results are shown in Fig. 5.

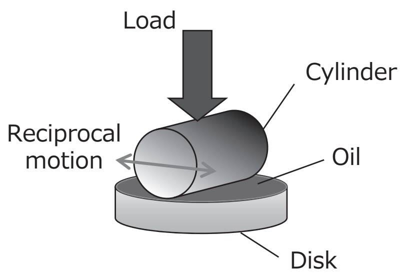

Fig. 4. Outline of cylinder-on-disk test

Table 3. Cylinder-on-disk test conditions

Cylinder	SCr415 (DLC-coated), φ33 mm × 22 mm
Disk	Al alloy or Cu alloy
Load	100 N
Reciprocal motion	Reciprocation frequency: 28 Hz, Amplitude: 3 mm
Oil	Engine oil (0W-16), 80°C, Presence of MoDTC
Time	30 min

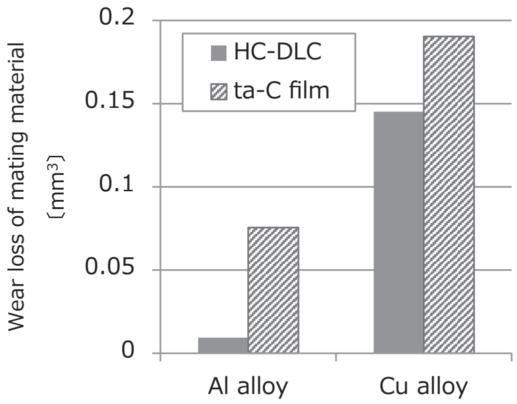

Fig. 5. Cylinder-on-disk test results

Compared with the ta-C film, HC-DLC wore Al and Cu alloys less significantly, when these metals were used as the mating members. This verified that HC-DLC exhibits lower attackability to the mating material than a ta-C film when sliding on a soft metal.

Prior to the test, the surface conditions of HC-DLC and the ta-C film were examined under a scanning probe microscope (SPM). Consequently, these films exhibited a large difference in the quantity of fine protrusions (Figs. 6 and 7), despite the fact that these films were lapped under the same condition. The probable reason is that the addition of a suitable amount of hydrogen to HC-DLC made removing the droplets easy and lowered the attackability of the new film to the mating materials.

3-4 Seizure resistance of HC-DLC film

To check the seizure resistance of HC-DLC, a seizure test was carried out using engine oil containing MoDTC (Fig. 8 and Table 4). In this test, the load was increased until the brass pin broke. The load when the brass pin broke was defined as the seizure load (Fig. 9).

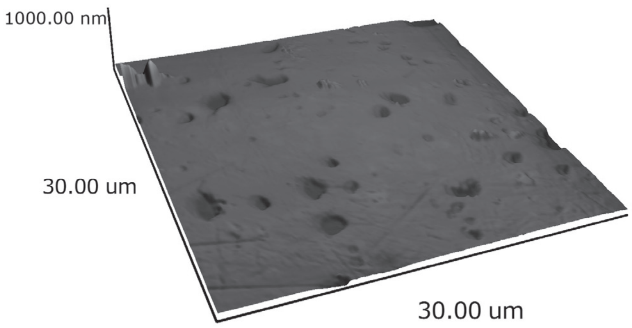

Fig. 6. SPM image of HC-DLC (surface roughness: Rz = 0.32 μm)

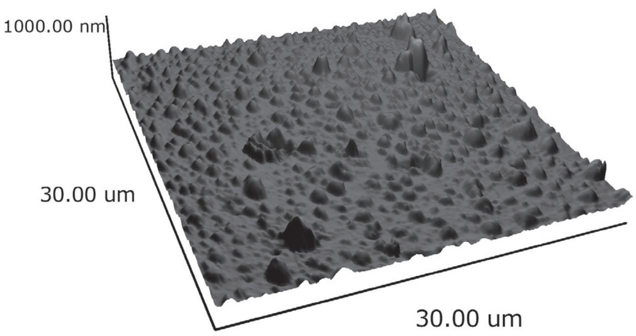

Fig. 7. SPM image of ta-C film (surface roughness: Rz = 0.70 μm)

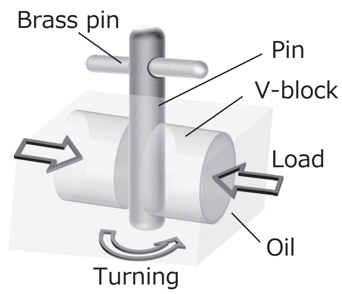

Fig. 8. Outline of seizure test

Table 4. Seizure test conditions

Pin	SAE 3135 (DLC-coated or uncoated)
V-block	AISI 1137
Load	Increased at a rate of 3 kN/min
Turning	500 rpm
Oil	Engine oil (0W-20), 80°C, Presence of MoDTC

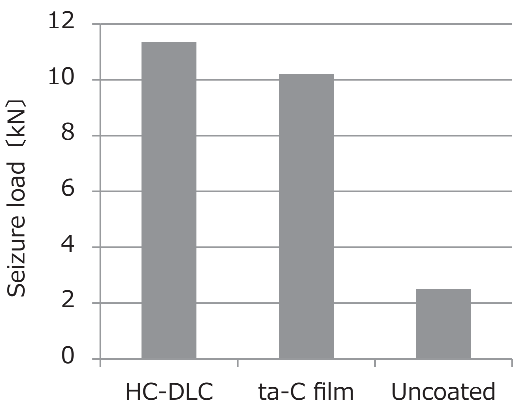

Fig. 9. Seizure test results

We confirmed from this seizure test that HC-DLC exhibits higher seizure resistance than ta-C films.

To investigate the reason, the test was suspended when the load reached 5 kN, and the surface condition of the DLC film was observed under a microscope. As a result, we found that, when compared with the ta-C film, HC-DLC demonstrated an extremely smaller number of scratch marks created by the droplets removed (Photos 1 and 2). The above result suggested that ease of droplet removal lowers the attackability of HC-DLC to the mating material and restricts the damage to the DLC film itself, thereby enhancing the seizure resistance of the new film.

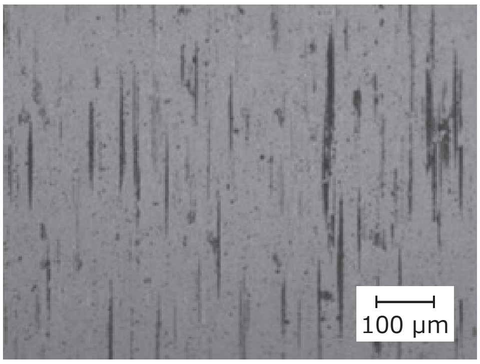

Photo 1. Surface of HC-DLC when the application of load was stopped at 5 kN

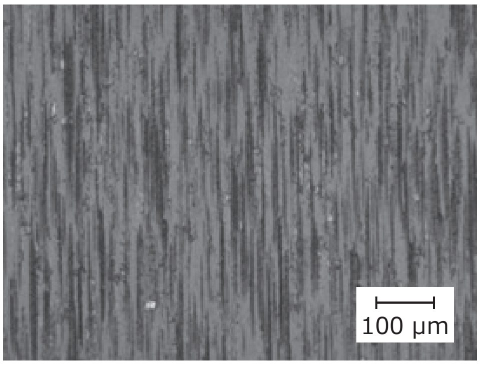

Photo 2. Surface of ta-C film when the application of load was stopped at 5 kN

4. Conclusions

Newly developed HC-DLC does not suffer abnormal wear, even in sliding conditions where a-C:H films are worn abnormally in the presence of MoDTC. Therefore, HC-DLC can be used even in sliding environments where oil containing MoDTC is used. Due to its lower attack-ability to soft metals and higher seizure resistance than ta-C films, HC-DLC is suitable as a protective film for piston pins and other engine parts that slide on soft metals.

Technical Terms

*1 DLC: An abbreviation for diamond-like carbon, a general term for amorphous thin films containing carbon as a major component.

*2 MoDTC: An abbreviation for molybdenum dithiocarbamate, a friction modifier that is widely used in engine oil.

*3 a-C:H: An abbreviation for hydrogenated amorphous carbon, a DLC film containing hydrogen. This film is called a hydrogenated amorphous carbon film.

*4 CVD: An abbreviation for chemical vapor deposition, a method in which a source gas is poured to deposit a film by a chemical reaction.

*5 ta-C: An abbreviation for tetrahedral amorphous carbon, a DLC film called a tetrahedral amorphous carbon film. This DLC film does not contain hydrogen and demonstrates a high diamond structure ratio.

*6 ta-C:H: An abbreviation for hydrogenated tetrahedral amorphous carbon, a DLC film containing hydrogen in ta-C. This DLC film is called a hydrogenated tetrahedral amorphous carbon film.

References

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