History and Applications of Diamond-Like Carbon Manufacturing Processes

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Diamond-like carbon (DLC) is a hard material with lubricity and chemical stability. Amid the growing awareness of environmental problems in late years, DLC films have been used to reduce the fuel consumption of automobiles by reducing friction loss. The films are also used as a coating of cutting tools for aluminum alloys that have been widely used for automobile weight reduction. Nippon ITF Inc. provides DLC films most suitable for the customer needs by utilizing its equipment, systems, and expertise. This paper introduces the history of DLC manufacturing processes and DLC films that we have commercialized.

Keywords: DLC, PVD, CVD, coating, low friction

1. Introduction

Diamond-like carbon (DLC) first appeared in a paper in 1971. DLC was discovered by accident during research on vapor-phase synthesis of diamond. In the 1950s, high-pressure synthesis of crystalline diamond was developed but it required special and expensive equipment. Therefore, a lot of research was conducted on vapor-phase synthesis for growing diamond crystals from hydrocarbon gas or carbon vapor (gaseous phase).(1) During this process, Aisenberg et al. published a paper on an amorphous hard film mainly composed of carbon in 1971, which was later called DLC.(2) After that, various DLC deposition processes and films were developed. Having superior characteristics as a lubricative material, such as a low coefficient of friction, high hardness, and chemical stability, DLC films have driven forward development in a unique way different from the vapor-phase synthesis of crystalline diamond. In particular, the low friction coefficient of DLC has been drawing attention due to the requirement to address environmental problems, and the importance of DLC has been increasing in reducing the fuel consumption of automobile engines by decreasing friction, being introduced as driving components and pump components to prevent seizure. Starting from the history of processes for producing DLC films, this paper introduces the classification techniques and features of the DLC films we have developed and their applications in this order.

2. DLC Deposition Processes and Their Features

The methods for producing DLC films are broadly divided into two types: Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). The PVD method uses a solid (graphite) as the carbon source and the CVD method uses a gas (a hydrocarbon such as methane). The PVD method is further divided into the arc, sputter, and laser vapor deposition methods. The CVD method includes radio-frequency (RF), direct-current (DC) discharge, Penning ionization gauge (PIG), and self-discharge methods. Figure 1 is a conceptual diagram showing the RF discharge plasma CVD, PIG plasma CVD, and arc PVD adopted by us.

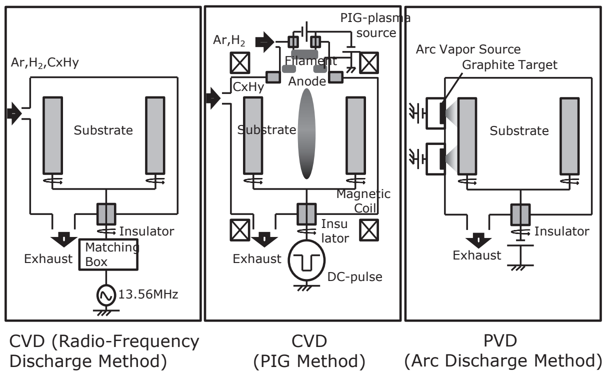


Fig. 1. Typical DLC Production Process

2-1 Radio-frequency discharge plasma CVD method

The methods for producing DLC by exposing a base material to glow discharge plasma of a hydrocarbon gas were actively studied in the latter half of the 1970s, and many papers were published until the first half of the 1980s.(3) The major methods for generating glow discharge in decompressed gas include the DC discharge and RF discharge methods. Many of them apply the high-frequency power or a negative DC voltage to the base material, which is the cathode, and the counter anode is kept at the ground potential. Acetylene (C_2H_2) or methane (CH_4) is used as the raw material gas. A DLC film containing hydrogen is obtained by emitting an active species such as ions and radicals*[1] in hydrocarbon gas plasma onto the surface of the base material kept at a relatively low temperature.

2-2 PIG plasma CVD method

This process also forms a DLC film by exposing hydrocarbon gas to plasma. However, since it can control the amount of carbon ions incident upon the base material and the energy of the incident carbon ions independently, it is classified as the remote plasma CVD method, which produces a DLC film containing hydrogen. This method allows the easy control of the thickness, hardness, residual stress, and composition of a DLC film. These features of the CVD method make the DLC film coating applicable to various shapes of a base material, allowing for a wide range of applications. In addition, plasma occurs in a wide range of conditions, and the input power and raw material gas can be used relatively efficiently. Although inferior in film hardness compared to the arc PVD method mentioned below, this method can form films with a wider range of characteristics than the RF method and can even produce DLC with a film thickness of 60 µm. Since the PIG method has flexibility in controlling the hardness and thickness of the film, it can form a film on soft metal base material such as aluminum.

2-3 Sputtering/Plasma CVD-composite method

The sputter vapor deposition method forms a carbon film on a base material by applying a DC voltage or high-frequency power to a sputter vapor source made of solid graphite, and making positive ions in inert gas plasma collide against graphite to pump out carbon atoms.(4) It can form a smooth DLC film, but has a disadvantage of a low film deposition rate due to a low carbon sputter yield. A DLC film can be formed in the same manner as the plasma CVD method by letting hydrocarbon gas flow into a furnace. The film deposition rate is significantly increased compared to the sputter vapor deposition method that does not use hydrocarbon gas. If metal is used as the sputter vapor source, a DLC film containing a metallic element can be produced. Sputtering with a simple graphite material is classified as a pure PVD method, and forms a DLC film without hydrogen. If a hydrocarbon gas is used, it is classified as a remote plasma CVD method, generating a DLC film with hydrogen.

2-4 Arc PVD method

The cathode arc PVD method forms a DLC film on the surface of a base material at a negative potential by generating a continuous vacuum arc discharge on the surface of a solid graphite cathode to efficiently generate carbon ions. This method was developed in the former Soviet Union, and creation of a DLC film that does not contain hydrogen was reported as early as in the 1970s.(5) Then, when this technology was introduced to Western nations in the late 1970s, the development was accelerated in Australia and Europe, and then in the United States. This process features easy formation of hard hydrogen-free DLC films that contain more diamond (sp^3-bonded carbon) and less graphite (sp^2-bonded carbon) because of the high vaporization and ionization rates of graphite. In addition, with a relatively small size vapor source, it is possible to form a film at a high speed on large base material by operating many vapor sources at the same time.

It has the disadvantage of film contamination with coarse particles, called droplets or macro particles, which are left unionized during arc discharge, resulting in an increase in surface roughness, increasing aggressiveness.

2-5 Filtered arc PVD method

As a means to prevent the coarse particles mentioned before from reaching the base material, a magnetic filter cathode arc vapor source that combines a geometrically bent duct and a magnetic field was developed in the former Soviet Union in the 1970s, and the deposition of a hard carbon film with a low number of defects was reported.(6) However, the magnetic filter reduces the utilization efficiency of the vapor source, which decreases the film deposition rate and processing area, resulting in a reduction in productivity. In addition, some coarse particles reflect inside the duct reaching the base material, and the equipment cost is high.

Table 1 shows the structure and characteristics of a DLC film formed by each process.

Table 1. Structures and Characteristics of DLC Production Processes

Process		DLC structure	Characteristics
Plasma CVD	Radio-Frequency Method	a-C:H (Hydrogen containing DLC)	Smooth and low friction (DRY) Able to form films against an insulating substrate Slightly low adhesiveness
	PIG Method	a-C:H (Hydrogen containing DLC)	Able to form thick films Controllable film thickness and stress Slightly inferior film thickness distribution
	Self Discharge Method	a-C:H (Hydrogen containing DLC)	Superior coverage Able to form internal coating High deposition rate and filling density Slightly low adhesiveness
PVD	Arc Method	ta-C (Hydrogen Free DLC)	Hardness close to diamong Low friction in oil Difficult to form thick films and sensitive to the surface condition
	Sputter Method	a-C, ta-C (Hydrogen free)	Supports conductive DLC Low hardness

3. DLC Classification Method

For DLC classification, Casiraghi et al. organized DLC types on a pseudo ternary phase diagram and clarified the relationship with deposition methods.(7) DLC films formed with the sputter vapor deposition method and arc PVD method do not contain hydrogen as long as only solid graphite is used as the raw material and no hydrocarbon gas is used. They are characterized by the differences in the amount of sp^3-bonded carbon and the structure of the cluster within the range from graphite-like carbon (GLC) that does not contain hydrogen and amorphous carbon (a-C) to tetrahedral amorphous carbon (ta-C) in Fig. 2. On the other hand, DLC films produced from a hydrocarbon gas using the plasma CVD method always contain hydrogen. These DLC films take the form of hydrogenated amorphous carbon (a-C:H) to hydrogenated tetrahedral amorphous carbon (ta-C:H), which are characterized by the differences in the amounts of hydrogen and sp^3-bonded carbon. Thus, DLC is distinguished by the amounts of hydrogen and sp^3-bonded carbon, and the cluster structure, which provides information for understanding various behaviors including mechanical (hardness and Young's modulus), optical (refraction, penetration/absorption), electric (conductance), and chemical (changes during an increase in temperature, oxidation, affinity with various materials) behaviors. For example, it has been reported that DLC containing a relatively high amount of hydrogen indicates an excessively low friction coefficient (0.02 or lower) in a dry nitrogen atmosphere and in an ultra-high vacuum, and that Si-added DLC has a low friction coefficient in a humid air atmosphere.[(8)] On the other hand, in the presence of lubricant oil widely used for automobile parts and mechanical components, the less the hydrogen content in a DLC film, the more the friction coefficient decreases.[(9),(10)]

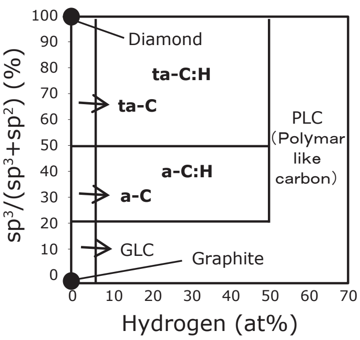


Fig. 2. Classification of DLC

4. DLC Films from Nippon ITF

Table 2 shows the classification and characteristics of typical DLC films from Nippon ITF, and Table 3 lists their characteristics and purposes.

Table 2. Characteristics of DLC Films from Nippon ITF

Grade name	Classifi -cation	Thick -ness (μm)	Surface Roughness Rz (μm)	Hard-ness (GPa)	Oxidation Temperature (°C)	Sub -strate	Young Modulus (GPa)
HA	ta-C	≤ 1	1.0 After lap 0.3	60-80	500	Steel WC-Co	600
HAX	ta-C	≤ 1	≤ 0.1	60-80	500	Steel WC-Co	600
HC	ta-C:H	≤ 3	1.0 After lap 0.3	40-60	350	Steel WC-Co	500
HT	a-C:H a-C:H:Si	1-2	0.1-0.5	15-25	300	Metal Ceramic	150
HP	a-C:H a-C:H:Si	1-10	< 0.2	15-25	300	Metal	150
HS	a-C:H a-C:H:Me	0.5-1.5	< 0.1	20-30	300	Metal	200
F	a-C:H	0.3-2	< 0.2	< 15	300	Polymer	< 150

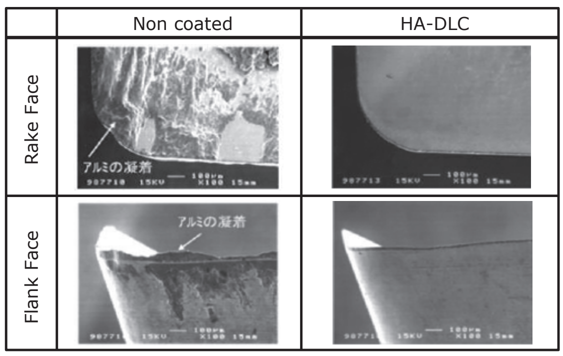
Table 3. Characteristics and Applications of DLC Films from Nippoin ITF

Grade name	Scratch Strength (N)	High Surface Pressure Sliding (N)	Characteristics	Typical Applications
HA	≒ 60	> 5000	High hardness Low friction in oil	Tools, molds for soft metals such as Al Engine components
HAX	≒ 50	> 5000	High hardness Low defect density	Precision molds Lens molds
HC	≒ 60	> 5000	High durability Able to form thick films	Engine components
HT	≒ 50	3000	Low internal stress	General machine parts Automobile parts (except engine)
HP	≒ 50	Not measured	Able to form internal coating	Internal coating of Pipe
HS	≒ 80	> 5000	Low aggressiveness	Automobile parts (except engine)
F	Not measured	Not measured	Low temperature treatment Supports polymers	Rubber parts (Low friction, Fixing prevention)

4-1 HA-DLC

HA-DLC films are formed with the arc PVD method and do not contain hydrogen. They are hard thin films classified as ta-C with a hardness second to diamond. They are used for tools for cutting aluminum alloys and molds, and are effective in preventing welding of soft metals and resins, improving processing accuracy, and extending life. These films indicate low friction in oil, and superior abrasion resistance even in oil containing a lubricant such as Mo-DTC. In 2006, they were applied to mass production as low-friction films for valve lifters, which are automobile engine components.

Figure 3 compares the results of cutting an aluminum alloy (ADC12) by a normal cemented carbide tool and a cemented carbide tool coated with HA-DLC. While the non-coated cemented carbide tool indicated an excessive adhesion of aluminum, the tool coated with HA-DLC had little adhesion. Figure 4 indicates the result of evaluating cutting forces. The tools coated with HA-DLC had lower cutting forces compared to a normal cemented carbide tool in both dry and wet conditions. This is because a DLC film is less likely to cause



Cutting conditions
Speed: 300m/min, Feed: 0.15mm/t,
Ad = Rd = 5mm, Length:9m, Work: ADC12
Tool: WEM3032E, APET160504PDFR-S
Machine: Makino Machining Center (V55)

Fig. 3. Adhesion Resistance in Cutting Aluminum

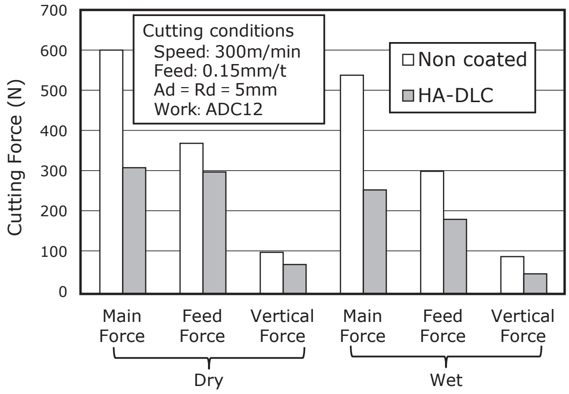


Fig. 4. Cutting Forces in Cutting Aluminum

aluminum adhesion and has a lower friction resistance, which smoothly discharges cutting chips.(11)

Figure 5 compares the friction coefficients of non-coated SCM415 carburizing material, TiN, hydrogen-containing DLC, hydrogen-free DLC (HA-DLC), and SCM415 material coated with diamond with a mating material of SUJ2 without lubrication and in oil. Without lubrication, the non-coated SCM415 and TiN indicated seizure, but the DLC and diamond-coated products did not have seizure. In oil, hydrogen-free DLC indicated low friction close to the diamond-coated product. This is because that HA-DLC is ta-C containing many sp^3-bonded carbon atoms similar to diamond, and oil has superior affinity with sp^3 components. The low friction in oil was the main reason for the adoption of HA-DLC in valve lifters, which are components of the dynamic valve system of an automobile engine.(9)

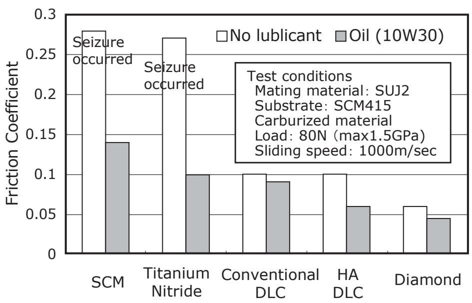


Fig. 5. Friction Coefficients of Various Films without Lubricant and in Oil

4-2 HC-DLC

HC-DLC films are formed by the arc PVD method and contain hydrogen. They are classified from the ta-C:H to a-C:H groups. These films can use not only solid targets but also a hydrocarbon gas as a raw material during film formation. They are less hard than HA-DLC and have less surface roughness than HA-DLC. Therefore, they are superior in chipping resistance and conformability, and have low aggressiveness. It is possible to create DLC films with different hydrogen contents, and to some extent, control film hardness by adjusting the input and pressure of hydrocarbon gas. The expected applications of these films include automobile engine components, as well as various machine parts, and molds for soft metals.

4-3 HT-DLC

HT-DLC films are formed with the PIG Plasma CVD method and contains hydrogen. They are classified into a-C:H. Since HT-DLC is suitable for any base material, and the structure and characteristics of the film can be controlled for a wide range of purposes, it is applied to automotive frictional parts and various other machine parts. The drive train parts of an automobile use lubricants and grease for smooth sliding. If the lubricant or grease deteriorates or is washed away, vibration or an unusual noise occurs, and in the worst case, seizure takes place. It is sometimes necessary to take wear preventive measures against dust entering from outside. In recent years, bioethanol fuels are sometimes used. Foreign materials from this fuel cannot be completely removed with a filter, which can cause wear of pump parts. These parts are made by casting alumite-treated aluminum for reducing weight and facilitating processing. The evaluation of various DLC films indicated that only HT-DLC films can be stably formed on insulating and porous alumite, and HT-DLC was adopted to the mass production of the parts of motorcycle fuel pumps.

4-4 HP-DLC

With the PIG plasma CVD method, it is difficult to homogeneously coat inside a pipe or a part with a complicated shape. The film-forming pressure of the normal plasma CVD method is about 0.1 to 10 Pa. In this range of pressure, the thickness of the ion sheath where almost no electrons exist is several tens of millimeters or more. For pipes thinner than this, high-density plasma was not generated inside, and DLC films could not be formed. To overcome this drawback, HP-DLC generates high-density plasma inside the hole by hollow discharge*2 to keep gas pressure at several tens of pascals or higher. Figure 6 shows the range of inner

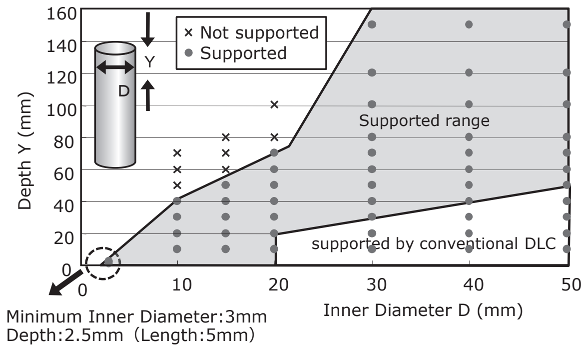


Fig. 6. Range of Depths and Diameters inside a Pipe that can be Coated with HP-DLC

diameters and hole depth for which films can be formed with HP-DLC. In the case of a pipe with both ends open, it is possible to process to a depth twice as that in the figure. HP-DLC can be applied to bearings, the inner surface of a cylinder, the holes of a mold, and the inner surface of a pipe for liquid or gas.

4-5 F-DLC

F-DLC films are formed with the RF plasma CVD method and contain hydrogen. They are classified into a-C:H. F-DLC was developed as a process that can coat polymers in particular. In general, DLC coating is performed after cleaning the surface of the base material by emitting Ar or other ions on the surface. Polymer materials have the problem of the rise in temperature during ion emission, negatively impacting their quality. F-DLC uses a method to remove stain on the base material at low temperatures by exposing the surface to hydrogen plasma. With normal plasma CVD methods, the temperature of the base material reaches nearly 200°C, impacting the quality of polymers. Therefore, plasma generation must be intermittently stopped to control temperature rise to 60°C to 80°C, which enables the deposition of DLC films with superior adhesion without deteriorating polymers. In addition, since polymer materials are soft and easily deformed, a normal DLC film cannot follow the deformation, and the film breaks. To prevent this, an F-DLC film has introduced cracks in the direction of its thickness. Photo 1 is a scanning electron microscope (SEM) photo of the surface of an F-DLC film. With the existence of cracks inside the film, the film does not break even if the base material is significantly deformed. Figure 7 shows the friction coefficients of the F-DLC films coated on various rubbers. The friction coefficients of the non-coated surfaces greatly differ between the types of rubber. However, if they are coated with F-DLC, they indicate low friction similar to polytetrafluoroethylene (PTFE). This low friction can be obtained even in dry environments, and great effects can be expected in environments where lubricant or grease cannot be used. Since DLC is chemically stable, and less likely to change in quality in different use environments (heat, oil, etc.) compared to rubber, it is expected to have suitability to preventing adhesion, which is an issue with rubbers.

Figure 8 shows the result of a ball-on-disc test on PTFE and PTFE coated with F-DLC. F-DLC coating reduces abrasion wear by approximately 1/9, with a friction coefficient similar to PTFE. F-DLC has advantages over PTFE in wear resistance and superior dimensional accuracy with a thin-film coating. In applications with a low load on sliding surfaces represented by a ring-on-disc test, PTFE coating indicates lower friction. For high-surface pressure (PV at 1,200 MPa·m/min or higher) and high-precision (1 to 10 μm) purposes, DLC should be selected, and for low-surface pressure (PV lower than 1,200 MPa·m/min) and low-precision (film thickness of 1 to 10 μm), PTFE coating is suitable.

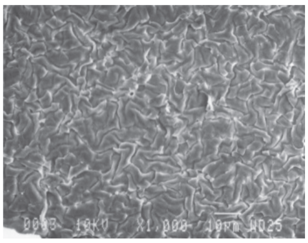


Photo 1. SEM Photo of F-DLC

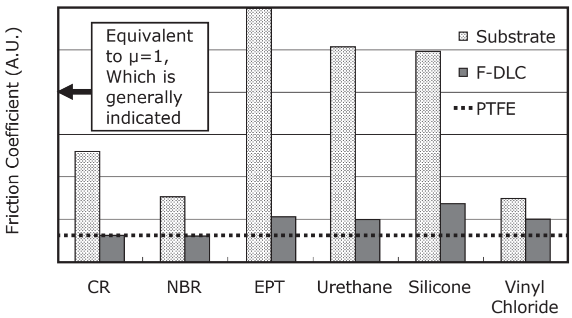


Fig. 7. Friction Coefficients of Various Rubbers Coated with F-DLC

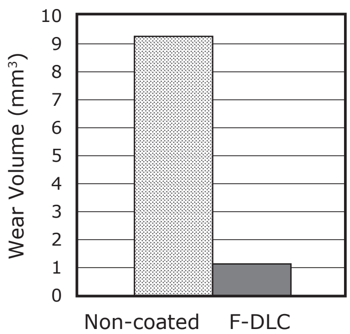


Fig. 8. Wear Characteristic of PTFE Coated with F-DLC

4-6 HS-DLC

HS-DLC films are formed with the sputtering/plasma CVD-composite method, and classified into a-C:H. Superior peel resistance and chipping resistance have been achieved by independently controlling the amount of carbon ions incident upon the base material and the energy of the incident carbon ions to form a DLC film with the quality gradually changing along the depth of the film and by introducing an intermediate layer with superior adhesion. An FZG test*3 of a gear coated with HS-DLC indicated no scuffing damage*4 up to the final 14th-stage in an oil environment without lubricant. HS-DLC has superior adhesion and chipping resistance compared to other plasma CVD films.

4-7 Latest DLC films

Nippon ITF has standardized HAX-DLC films formed with the filtered arc method. HAX-DLC films have overcome the disadvantage of HA-DLC in surface roughness. However, the film deposition range and film deposition rate are limited because of the use of a deflecting magnetic field. With an intention of solving this drawback, Nippon ITF worked to develop an arc vapor source with no coarse particles, and succeeded in developing a film deposition process that generates almost no coarse particles. Photo 2 is a SEM photo of a DLC film formed using this process. Compared to HAX-DLC, the DLC produced with the new process is superior in smoothness, film deposition range, and film deposition rate, which are comparable to those of the normal arc film-deposition process. As this new hydrogen-free DLC film deposition process significantly suppresses the generation of coarse particles and eliminates the need for post-polishing, efforts are being made to establish it in mass production, targeting the lens mold market that places prime importance on surface smoothness and thermal resistance. Future application to cutting tools, automobile/machine parts, and electric/electronics components is also being considered.

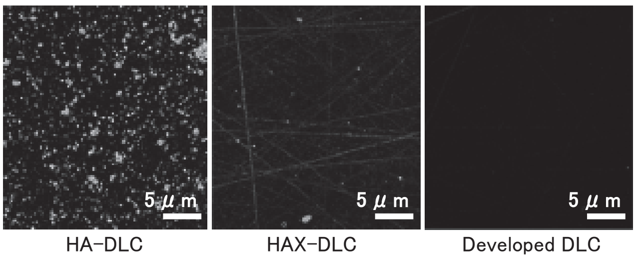


Photo 2. SEM Photos of DLC Produced by Various Arc PVD Method

5. Conclusion

Thanks to its superior lubrication characteristics, the application of DLC has been expanding to a wide range of industries. In recent years, due to the environmental and fuel efficiency regulations in the automobile field, DLC coating is drawing attention as an important technology for reducing power loss. Hydrogen-free DLC in particular, in which Nippon ITF has strength, has become the focus of attention for its superior wear resistance in a lubricant containing Mo-DTC*5 in application to automobile parts including not only valve lifters but also piston pins and piston rings. As various regulations become tighter, the needs for DLC films superior in sliding characteristics are expected to increase.

To respond to these expectations, it is necessary to develop films suitable for their applications, processes that support various part shapes, and technology for reduction of costs. For application to parts in practical use, it is becoming more important to comprehensively examine the compatibility with the base materials of the parts and the using environments before designing the characteristics and structure of the DLC films. Therefore, it is also necessary to select base materials and design shapes according to the target DLC by cooperating with the design, manufacturing, and development divisions of the users who will apply DLC films. Such cooperation and partnership will become increasingly important.

Technical Terms

*1 Radical: Atoms and molecules having unpaired electrons, rich in reactivity.
*2 Hollow discharge: Electric discharge caused by electrons enclosed in a small space moving intensely back and forward.
*3 FZG test: A gear evaluation method developed in Germany.
*4 Scuffing damage: Scratches, which appear as a precursor to seizure.
*5 Mo-DTC: Molybdenum Dialkyl Phosphorodithioate, which is added to oil to server as a lubricant.

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