Application of Diamond-Like Carbon to a Rotary Engine

Tatsuyuki Nakatani*,1, Keishi Okamoto, Atsunori Araki and Tomohiro Washimi

Toyo Advanced Technologies Co. Ltd. 5-3-38 Ujina-higashi, Minami-ku, Hiroshima 734-8501, Japan
1Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo Machi, Nagasaki 852-8521, Japan

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To reduce wear in automobile-application rotary engines and extend their life, the authors proposed that diamond-like-carbon (DLC) coating, which has superior tribological properties, is applied to a rotary engine part (corner seal). Since wear resistance is required for the surface, the film must be hard. Additionally, in consideration of the high temperature due to the part being next to the combustion chamber, it is desired that the entire film has high heat resistance. To form a DLC film that has multiple properties including heat resistance, adhesion, and wear resistance required by the engine part, the authors discovered that it is possible to control the film’s hardness and heat conductivity via its Si content, and by producing a gradient of Si content in the film, they succeeded in realizing both hardness of the surface and heat resistance throughout the film, thus enabling the practical use of such a rotary engine part (corner seal).

1. Introduction

The attention of the world seems to be focused on environmental issues and, in particular, the seriousness of energy issues related to oil. Given the impact that such issues have on the automobile industry, all companies are promoting the development of hybrid vehicles, fuel cell vehicles, and next-generation vehicles as well as the improvement in fuel efficiency. Figure 1 shows a rotor housing and an equilateral-triangle-shaped rotor in a rotary engine.
The environmentally friendly concept of rotary engines, the pride of Mazda Motor Corporation, matches this worldwide trend, and its evolution continues to progress toward further improvements in fuel efficiency and maintenance-free, long-life engines. In the rotary engine, the rotor shaped like a triangular rice ball is placed in rotor housing with an elliptical shape. Rotary engines are superior to reciprocating engines in terms of performance owing to their unique structure that directly utilizes the rotation of the rotor, and offer advantages such as a lightweight and compact design, less noise and vibration, and high power. As a result of further improvements in such engines, the next-generation rotary engine “RENESIS,” used in the current version of the Mazda RX-8, has been developed. In the development of “RENESIS,” strict conditions were imposed on the new design and on all parts with the aim of improving fuel efficiency and extending engine life. For example, by adopting innovative technologies including a side-exhaust port system, higher power was achieved, together with improved fuel efficiency and a cleaner exhaust gas in comparison with conventional rotary engines. In this paper, we introduce an actual case where diamond-like carbon (DLC) was applied to the corner seals shown in Fig. 2 as a measure for extending their product life span.

2. Problem Regarding Wear in Rotary Engines

In terms of wear in rotary engines, the most critical parts are apex seals, side seals, and corner seals, which are gas seals. Apex seals and side seals are installed, respectively, on the three edges and six edges where the rotor comes into contact with the rotor housing, and
they are directly in contact with the rotor and side housing in order to seal the combustion chamber. In other words, if the seals are worn out, incomplete combustion caused by gas leakage occurs, negatively affecting fuel efficiency. These seals are supported by springs so that force is constantly applied, whereas some degree of freedom of movement is granted in the vertical direction to absorb impacts arising from contact. Corner seals are installed at both ends of apex seals to provide this freedom, and protect the apex seals. Although corner seals move in synchronization with apex seals, they slide on the main body of the rotor, and the sliding surfaces wear on both sides. In the past, hard chrome plating was applied to corner seals. Chrome plating is applied to many mechanical parts because it can significantly extend part life span at a low cost. It is also applied to many parts in engines. As a matter of course, hard chrome plating is applied to many parts including corner seals in rotary engines. However, because hard chrome plating on corner seals is not sufficient by itself to extend part life span, it was proposed that a DLC coating, which has good sliding properties, is applied. This reasoning is clear given that the coefficient of friction of hard chrome plating is 0.42, whereas the coefficient of friction of DLC is 0.1. In addition, wear on the rotor main body, the complementary part, can be reduced. Although a single-layer DLC coating was also considered instead of hard chrome plating, a laminated concentration-gradient-type heatproof DLC film, which was made by coating hard chrome plating with DLC, was adopted because this increased the life span of the DLC more than the conventional hard chrome plating for additional protection.\(^{(1)}\)

3. **Properties of DLC Films**

In the last ten years, practical applications of DLC have significantly developed. It is used in a wide range of applications including household faucet fittings, acoustic equipment, semiconductor manufacturing processes, cutting processes, various forming processes, and other familiar applications. In addition, because of its superior sliding properties, DLC is expected to be applied to sliding parts in automotive engines, and components such as injection nozzles for diesel fuel injection pumps.\(^{(2)}\)
Because DLC consists of carbon atoms similar to those in diamonds, DLC films are generally harder than other hard thin-film coatings. Whereas the nanoindenter hardness of diamond is approximately 50 to 100 GPa, the hardness of DLC is approximately 25 to 50 GPa. This hardness is at least three times higher than that of hard chrome plating (10 to 13 GPa). In addition, DLC is considered to have an sp³ hybridized orbital, such as in diamonds, and an sp² hybridized orbital, such as in graphite, in an amorphous structure without long-range order. The basic properties of DLC depend on the structural ratio and hydrogen concentration. In addition, DLC with other elements added can be also produced, and DLC with various properties can be produced depending on the additive elements and their quantities. Materials that are generally called DLC include a wide range of materials with varying compositions and additive elements.

Our company achieved a dense surface property by optimizing coating processes and coating conditions. This dense surface property exhibits superior tribological (friction and wear) properties, and has a low coefficient of friction that is a quarter of or less that of hard chrome plating. In addition, it also exhibits superior sliding properties that reduce the “wear and seizing of complementary parts.”

4. DLC Coating Conditions

Various DLC coating methods have been developed, and their characteristics and properties often vary in accordance with production methods. Therefore, it is necessary to use a method that is suitable for the intended application and purpose. For industrial applications, plasma-enhanced chemical vapor deposition (PECVD) and ionized deposition methods are often used. Ionized deposition was used when DLC was applied to corner seals. The ionized deposition system used was a regular one that introduces argon, which is the ion source, plus a hydrocarbon gas such as benzene (C₆H₆), into a DC arc discharge plasma source installed inside a vacuum chamber, and causes the plasma thus generated to bombard a surface biased to a negative voltage, thereby forming a solid DLC coating on the surface. The advantage of this method is that since ionized hydrocarbons are accelerated by DC bias, hydrogen is expelled from the film, and consequently the film hardens. DLC coating conditions for corner seals were as follows. Hydrocarbons, including C₆H₆ and C₂H₂ and gases, including tetramethylsilane (Si(CH₃)₄), were used. The treatment temperature was at 200°C or less. The bias voltage was 1.0 kV or more. The pressure in the furnace was approximately 0.1 Pa. Under such conditions, a coating rate of 1 μm/h was obtained. Figure 3 shows an image of DLC coating applied to corner seals in a furnace. Additionally, as shown in Fig. 4, to improve the adhesion of DLC to the base material, a DLC coating containing Si was formed that possessed a concentration gradient in which the area near the interface with the hard chrome plating served as a low-Young’s-modulus region (layer). This was also in order to avoid any interface formations between different materials and stress concentration arising from rapid changes in materials. The film thickness of DLC on corner seals was 1 μm, and a film surface hardness of 29 GPa was obtained.
5. Evaluation of Heat Resistance of Toyo DLC

The application of DLC to the inside of a rotary engine presents a thermal problem as well as a wear problem of sliding parts, including corner seals. DLC films are not suitable for high-temperature applications, because their structure changes from an amorphous one to a graphite structure as temperature is increased. Typically, the heat resistance temperature of DLC is approximately 300 to 400°C. When DLC is applied to the inside of an engine, a temperature of approximately 1000°C in the vicinity of the spark plug causes the degradation of DLC due to heat, although this is not peculiar to rotary engines. In order to prevent such
thermal degradation, Toyo has developed a laminated concentration-gradient-type DLC with superior heat resistance.

Four types of DLC films including D@DLC, A@BLC, BHeatproof BLC, and C@CSPAT CORT, which are product names of Toyo, are discussed below. These four types of films are primarily different in Si content. The amounts of Si in films of D@DLC, A@BLC, BHeatproof BLC and C@CSPAT CORT are approximately 0%, 3.0%, 19.0% and 26.8%, respectively. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) were used to measure the Si content in the DLC films. ERDA is generally used to measure the amount of hydrogen in DLC films, but here it was used to measure the Si and hydrogen contents simultaneously in order to determine the relation between the Si and hydrogen contents. For measuring devices, an RBS end station (RBS-400) made by CE & A was used for RBS, and a Pelletron-type 1 MV tandem accelerator made by NEC Corporation was used for ERDA. For RBS, He\(^{++}\) ions with an energy of 2.275 MeV were incident on a sample at an angle of 75° with respect to the normal to the sample surface, and scattered He atoms were detected at an angle of 160° using a semiconductor detector. After that, when measuring the hydrogen content in DLC films by ERDA, He\(^{++}\) ions with an energy of 2.275 MeV were incident on the sample at an angle of 75° with respect to the normal line to the sample surface, and scattered hydrogen atoms were detected at an angle of 30° using a semiconductor detector. For a forward-scattering detector, a thin foil was used to remove He atoms scattered from the sample simultaneously with forward-scattered atoms. Furthermore, in the measurement of Si content, average and overall structure, evaluations were carried out as a cross check, using an Auger electron spectroscope made by Physical Electronics, Inc.

5.1 Heat resistance properties

Heat resistance tests were carried out using four superhard test pieces (12 × 12 × 6 mm), on which the above films D@DLC to C@C were formed. The test method was as follows. After the temperature in the furnace was changed as shown in Fig. 5 (the temperature was maintained at 500°C for 3 h), the states of the test pieces before they were put in the furnace (before treatment) were compared with their state after they were put in the furnace (after treatment).

Although no differences between before and after treatment were found as a result of a visual check, by using a laser microscope, cracking could be observed as shown in Fig. 6,

![Fig. 5. Temperature change in furnace during heat resistance test.](image-url)
and it was possible to observe differences in Si content and the occurrence of cracks. A pinhole confocal laser microscope (VK-9500, Keyence Corporation) was used. It was found that the 0%-Si film was strongly degraded by heating to 500°C. In contrast, no cracks were found on 19.0%-Si and 26.8%-Si, and no significant surface changes were observed after the treatment. A similar observation was carried out after the temperature in the furnace was increased from 500°C to 600°C. Although a slight increase in the number of cracks was found on 3.0%-Si, no cracks were found on 19.0%-Si and 26.8%-Si. A summary of the results is shown in Table 1. From these results, it can be concluded that test pieces that have a higher Si content are not degraded by heat. In other words, they have superior heat resistance.

5.2 Relationship between heat conductivity properties and heat resistance properties

Heat conduction means that heat is conducted (moved) from the hot side to the cold side, and this movement is carried out by phonons (lattice vibrations) and conduction electrons. In metals, conduction electrons primarily conduct the heat, and diamond is the best material in the world in terms of heat conductivity, having heat conductivity of around 1,000 w/m·k. In diamond, phonons primarily conduct the heat, and heat vibrations can be transmitted with little damping because of the regular crystalline orientation. Conversely, materials that have low heat conductivity are nonmetals, which have a disordered lattice arrangement. Since DLC is a nonmetal and has an amorphous structure, it exhibits significantly low heat conductivity of around 0.7 w/m·k, although it resembles diamond.(7,8)

Comparison measurements of the heat conductivity of 0%-Si, 3%-Si, and 26.8%-Si were carried out. The scanning laser-heating AC method was used for the measurements.(9) Via a polygon mirror, AC heating, which uses the Laser PIT-R made by ULVAC Inc., was applied to the sample surfaces using a band of laser light 7.5 nm long by 0.5 mm wide, so as to scan the DLC-coated 30-μm-thick borosilicate glass samples. The responses of the AC heating temperature with regard to displacements from the thermocouples fixed in the samples were measured. The thickness of each sample’s film was 0.5 μm. Heat conductivity was determined using a thermal conduction equation on the assumption that the volumetric specific heat of the samples was equal to that of glass board.

Fig. 6. Photomicrograph of cracks (Photograph: Cracks on 0% Si).
The measurements were carried out three times for each sample, and an average value was then calculated. Figure 7 shows the relationship between heat conductivity and Si content that was thus obtained. It is found that an increase in Si content causes a decrease in heat conductivity. Additionally, as already shown in § 5.1, an increase in Si content causes an increase in heat resistance. Hence, the relationship between heat conductivity and heat resistance could be determined, and the result obtained was that a decrease in heat conductivity causes an increase in heat resistance.

6. Evaluation of Wear Resistance of Toyo-DLC

Next, in relation to the wear problems of rotors, the hardness, viscosity, and adhesion of films A to C are evaluated in terms of Si content.

6.1 Hardness

The hardnesses of films A to C were measured. In order to measure the hardness of the DLC film surfaces, a triangular-pyramid diamond indenter with an angle of 90° was used with a nanoindentation system equipped with a high-sensitivity (0.0004 nm, 3 nN) sensor made by Hysitron, Inc. The measurement conditions were as follows. The diamond indenter was pressed on a sample while it was controlled with an accuracy of 100 μN. Mechanical properties including hardness and modulus of elasticity were quantified on the basis of load-displacement curve analysis. The pressing time for the indenter was set at 5 s, and the drawing time was also set at 5 s.

Figure 7 shows the relationship between the hardness and Si content. This figure indicates that Si content reaches a minimum hardness in the range of 10 to 20%, and then the hardness increases with increasing Si. This shows that it is possible to control the hardness and heat conductivity by means of the Si content in the DLC film.

6.2 Relationship between Si content and hydrogen content

For films A to C, the hydrogen content of each film was measured by ERDA, and the measurement was carried out simultaneously with that of Si content.

Figure 8 shows the relationship between the hydrogen and Si contents in films A to C.
The figure indicates that there is a correlation between the hydrogen and Si contents in films, and that an increase in Si content causes an increase in hydrogen content. When the hydrogen content in a film is increased, the number of locations for forming covalent bonds is decreased because of the hydrogen bonds. Therefore, as hydrogen content is increased, film hardness is typically decreased. However, from Fig. 7 and Fig. 8, it is clear that the hardness of DLC films does not depend on only hydrogen content. Since an increase in Si content causes an increase in the number of Si-C bonds, it is inferred that the Si-C bonds are in a strong bonding state. As a result, the hardness of DLC films also depends on Si content.

6-3 Ratio between Si content and $I_G/I_D$ and Young’s modulus

The crystalline structure of DLC is amorphous under X-ray diffraction and electronic diffraction, and DLC films are basically a mixture of a soft graphite component (sp² bonding component) and a hard carbon component (sp³ bonding component). As the integrated intensity ratios of spectra ($I_G/I_D$) can be correlated with the sp²/sp³ bonding ratios, Raman
spectroscopy is a very effective method for evaluating the chemical structure of DLC. Raman-scattering spectroscopic analysis was carried out on films to . In this analysis, crystal lattice size can be evaluated through spectral analysis, because a difference in crystal structure causes a difference in the Raman spectrum. The ratio tendencies between sp² and sp³ orbitals for DLC films were evaluated on the basis of the relationship between the area ratio of G-band peaks to D-band peaks that could be separated from Raman spectra through curve fitting, on the one hand, and the Si content and Young’s modulus on the other. In this evaluation, DLC surfaces were analyzed using a microscopic laser Raman spectrophotometer (NRS-3200, Jasco Corporation). The measurement conditions are as follows. The excitation wavelength is 532 nm. The laser power is 10 mW. The number of diffraction gratings is 600 lines/mm. The magnification of the objective lens is 20×. The dimension of the slit is 0.1 × 6 mm. The exposure time is 60 s. Integration is made twice. Under such conditions, the curve-fitting process (band resolution) was applied to the measured spectra to determine the \( I_G/I_D \) ratios. Figure 9 shows the measurement results of to . From these it is evident that the higher the Si content, the larger are the integrated intensity ratios (\( I_G/I_D \)) of the Raman spectra.

Figure 10 shows the relationship between \( I_G/I_D \) ratio and Si content in films to and also shows the relationship between Si content and Young’s modulus obtained through nanoindenter hardness measurement. As shown in this figure, when \( I_G \) becomes larger than

![Fig. 9. Raman measurement results (left: DLC, \( I_G/I_D = 0.46 \) right: Cspat coat®, \( I_G/I_D = 1.13 \)).](image)

![Fig. 10. Relationship between Si content, \( I_G/I_D \) ratio, and Young’s modulus.](image)
$I_D$, the films become partially graphite, and consequently start to possess elasticity. This is also indicated by Young’s modulus obtained using a nanoindenter. Since an increase in Si content causes a decrease in Young’s modulus, the amount of strain corresponding to a constant stress becomes larger. In other words, it is found that the films start to possess elasticity.

Generally speaking, the greater the formation of the $sp^2$ bonding component in the DLC film, the more the graphitization will advance, and hence, the further the Young’s modulus will fall and the more elastic the film will become. In addition, the integrated intensity ratios ($I_G/I_D$) of spectra are correlated with $sp^2/sp^3$ bonding ratios.\(^{(10)}\)

Although evaluation of the $I_G/I_D$ ratios and $sp^2/sp^3$ bonding ratios by means of Raman spectroscopy in the visible wavelength region is known to entail difficulties, it can be concluded from the results of such evaluation that the $I_G/I_D$ ratios and Young’s modulus have correlations to the Si content of the DLC film, and that as the $I_G/I_D$ ratios increase, the formation of the $sp^2$ bonding component in the DLC film becomes large, as is clear from Fig. 10.

7. Evaluation of Improved Adhesion to Chrome Plating

Typically, the adhesion of a DLC film to a base material is not high, although this depends on the coating methods and conditions. The adhesion is also not high for DLC films formed on the chrome plating of corner seals. The adhesion varies with the conditions of the hard chrome plating, and is not stable over the mass production of several thousand pieces. Figure 11 shows the results of scratch tests for adhesion. First, for a nondefective test item (the upper part of Fig. 11), the DLC film was linearly peeled around the scratch trace. When a load of 50 N was applied, peeling occurred along the scratch trace, and the surrounding plating cracked in the area near the applied load. This shows that adhesion of the DLC film is very low in areas where the plating cracked. It is thought that this is because the DLC film could not be made that allows for elastic deformation when the load was applied, because the cracked areas appeared in the film. For the next defective test item (the middle part of Fig. 11), flakes were found in the area of the scratch mark and the surrounding areas. When a load of 50 N was applied, flakes were found on the surface in almost all the area of the scratch mark and the surrounding areas where the load was applied. This shows that the adhesion was clearly lower than that of the nondefective item, and that flakes were found not only in the areas of plating cracks, but also in the surrounding areas. It is considered that this is because impurities were generated owing to outgassing from the areas of plating cracks during the formation of the DLC film, and that the surface was consequently contaminated by these impurities. For reference, a scratch test was also carried out for a DLC film on a base material of high-speed steel (the lower part of Fig. 11). Flakes were found only in the area of the scratch mark. Also in the vicinity of the location to which a load of 50 N was applied, flakes were found only in the area of the scratch mark. It is thought that this occurred because the DLC film could not be made that allows for the elastic deformation, because the base material could not withstand the scratch load. As a result, the fundamental adhesive power of DLC films has been obtained. This result indicates that it is difficult to form a DLC film on hard chrome plating. The impurities that were found in the areas of plating cracks
in the scratch test of the defective item are considered to be a plating solution, an antirust material, a compound for barrel polishing, and similar materials. Since rust was actually found on the surface of the defective item, it is thought that a residue of the plating solution causes the spread of rust on the surface, and that, consequently, the DLC film flakes off. In addition, it is also thought that particles and impurities accumulate in the areas of cracks and cause poor adhesion of DLC films.

Accordingly, process improvements including enhancement of the cleaning process before coating and evaporation of unwanted impurities at 200°C or less have been implemented. In addition, pursuant to the results in Fig. 10, a low-Young’s-modulus region (layer) has been formed in the area near the interface with the hard chrome plating by giving such area a high Si content, in order to ameliorate the problem of the DLC adhesion to the base material. Because of this, formation of interfaces between different materials, or stress concentrations, etc., arising from rapid changes in material properties can be averted, and adhesion is enhanced. As a result of these improvements, stable adhesion of DLC has been achieved in actual mass-production corner seals.

8. Result of Application of DLC to Rotary Engine

In terms of wear and heat resistance, high hardness is required for the DLC film surface application to a rotary engine because DLC surfaces must have wear resistance, and heat resistance is required for the base material side of the film, because heat is conducted mainly from the base material side to the DLC film. However, since the temperature is high throughout the entire rotor, it is desirable that heat resistance is also high throughout the entire film. Therefore, on the basis of the relationship between Si content and heat resistance, films that have superior heat resistance properties can be obtained by gradually decreasing
the Si content from the base material side to the film surface. The film surface has a low Si content due to the gradual decrease in Si content, and high hardness can be obtained on the film surface. In addition, because the base material side has a high Si content, a film that has high hardness because of the Si-C bonds can be obtained. Furthermore, adhesion can be improved, because the base material side has a higher sp² orbital ratio, or because high elasticity can be obtained by causing the film to become partially graphite. On the basis of these results, a DLC film that has a superior heat resistance has been successfully obtained by optimizing coating conditions and adopting a concentration-gradient-type DLC.

For measures against wear on the circumference of the corner seal, a significant improvement has been achieved by DLC coating. Figure 12 shows comparative amounts of wear (on average) measured after various endurance tests for hard chrome plating only and for the same plating laminated with DLC film. The result shows that the wear of the sample coated with a concentration-gradient-type heatproof DLC is one tenth or less that of a sample that is not coated. This has enabled the development of the RENESIS next-generation rotary engine and the introduction of the RX-8 to the market.

9. Conclusion

On the basis of the relationship between Si content and heat resistance, films that have superior heat resistance properties can be obtained by gradually decreasing the Si content from the base material side to the film surface. The film surface has a low Si content owing to the gradual decrease in Si content, and high hardness can be consequently obtained on the film surface. In addition, a film that has high hardness because of the Si-C bonds can be obtained because the base material side has a high Si content. Furthermore, because the base material side has a higher sp² orbital ratio, or because high elasticity can be obtained by causing the film to become partially graphite, adhesion has been improved. On the basis of

Fig. 12. Comparison of wear after endurance test.
these results, by optimizing coating conditions and adopting a concentration-gradient-type DLC, a DLC film with superior heat resistance has been successfully obtained. The comparative wear measured after an endurance test for hard chrome plating only and for the same plating laminated with DLC film show that the wear of a sample coated with a concentration-gradient-type heatproof DLC was one tenth or less that of uncoated sample.

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