論文 / 著書情報
Article / Book Information

論題(和文)	
Title	Estimation of DLC wear process by micro laser Raman microscopy
著者(和文)	川口 雅弘, 青木 才子, 三尾 淳, 森河和雄, 内田聡, 崔埈豪, 加藤孝久
Authors	Masahiro Kawaguchi, Saiko Aoki, Atsushi Mitsuo, Kazuo Morikawa, Satoshi Uchida, Junho Choi, Takahisa Kato
出典 / Citation	Tribology online, Vol. 3, No. 2, pp. 110-115,
Citation(English)	Tribology online, Vol. 3, No. 2, pp. 110-115,
発行日 / Pub. date	2008, 4
権利情報 / Copyright	本著作物の著作権は日本トライボロジー学会に帰属します。 Copyright (c) 2008 JAPANESE SOCIETY OF TRIBOLOGISTS

Tribology Online
Japanese Society of Tribologists

Tribology Online, 3, 2 (2008) 110-115.
ISSN 1881-2198
DOI 10.2474/trol.3.110

Estimation of DLC Wear Process by Micro Laser Raman Spectroscopy

Masahiro Kawaguchi[1)*], Saiko Aoki[1)], Atsushi Mitsuo[1)], Kazuo Morikawa[1)], Satoshi Uchida[1)],
Junho Choi[2)] and Takahisa Kato[2)]

[1)]Advanced Material Processing Group, Tokyo Metropolitan Industrial Technology Research Institute
3-13-10 Nishigaoka, Kita-ku, Tokyo 115-8586, Japan
[2)]Department of Mechanical Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
*Corresponding author: kawaguchi.masahiro@iri-tokyo.jp

(Manuscript received 4 January 2008; accepted 13 March 2008; published 15 April 2008)
(Presented at JAST Tribology Conference Saga, September 2007)

In order to estimate the wear process of diamond-like carbon (DLC) films, a ball on disk test and a micro laser Raman spectroscopy are employed in this study. DLC films are deposited on high-speed tool steel (JIS-SKH51) surfaces by a plasma based ion implantation and deposition (PBII&D). After the ball on disk test with a steel ball (JIS-SUJ2) as an indenter, a mapping measurement using micro laser Raman spectroscopy has been accomplished against both the wear surface of the DLC films and the surface of the indenter. As a result, obvious changes in the structure of the DLC films originating from the contact interface between the substrate and the indenter are observed. This is like to be caused by the graphitization of the DLC films. On the other hand, except for the preceding descriptions, the Raman spectra are almost same to each other and there are no changes in the structure of the DLC films. This means that the effects of the sliding on the changes in the structure can be neglected. In addition, the carbon compounds and the solid solutions of carbon and iron included in the substrate and the indenter hardly influence the Raman spectra with or without sliding.

Keywords: diamond like carbon (DLC), PBII&D, micro laser Raman spectroscopy, graphitization, wear

1. Introduction

Recently, the scientific and technological interest towards hard amorphous hydrogenated carbon coatings (Diamond-Like Carbon; DLC) has been continuously increasing because of their extraordinary properties such as high mechanical hardness, low friction and high wear resistance. These properties are promising for a wide range of applications which require low-friction coefficient and high wear-resistance[1-5)]. On the other hand, variety of coating procedures of DLC films, which include physical vapor deposition (PVD), chemical vapor deposition (CVD), magnetron sputtering (MS), arc ion plating (AIP) and so on, have made deep understanding about the wear processes of DLC films as the film structure, mechanical properties, tribological properties etc. are mainly dominated by the coating procedures and conditions. Since the tribological conditions according to customer's usage are special and widely different and there are no standards established, a method for investigating the tribological properties by the industries[6-9)] and the means for estimating the tribological properties of DLC films are difficult to select. In addition, there are a few papers to discuss the relations between the tribological phenomenon and the changes in the structure of DLC films although there are many papers to discuss the friction and wear performance of DLC films. Therefore it is very important to study the changes in the structure of the DLC films during sliding.

In this study, DLC wear process has been estimated from the measurements of micro laser Raman spectroscopy. The change in the structure of DLC films by a sliding test can be analyzed by the Raman spectroscopy with focused laser beam of about 5 μm in diameter. It is considered that the estimation by the Raman spectroscopy as one of the standard methods is effective in order to clarify the DLC wear process.

2. Experimental setup

A high-speed tool steel corresponding to SKH51 in accordance with the Japanese Industrial Standards (JIS) is used as the substrate. The substrates are polished to a mirror-like surface using diamond powder. The deposition of DLC films is accomplished by the plasma based ion implantation and deposition (PBII&D) system with a single feed-through[10,11)]. The schematic illustration of PBII&D is shown in Fig.1. Both the radio

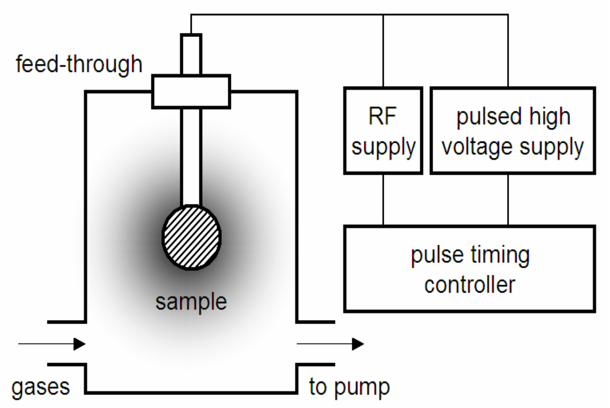


Fig.1 Schematic illustration of PBII&D

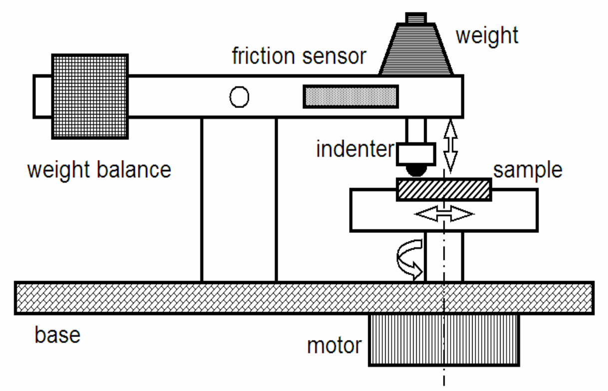


Fig.2 Schematic illustration of ball on disk tester

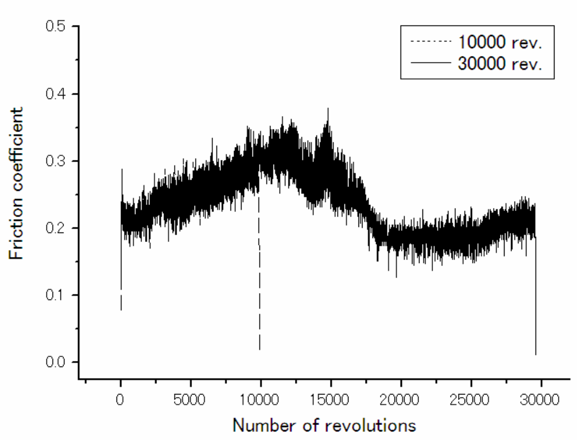


Fig.3 Results of sliding test

frequency (RF) and the negative bias voltage (HV) are driven as the high frequency pulses. The applied RF power, the RF duration, the pulse frequency and the HV are fixed at 500 W, 20 μs, 1 kHz, and 20 kV respectively. The gas pressure of CH_4 as a precursor is fixed at 1.0 Pa. The HV pulse frequency and width are 2 kHz and 10 μs respectively. The PBII&D process time is 3 hrs. The

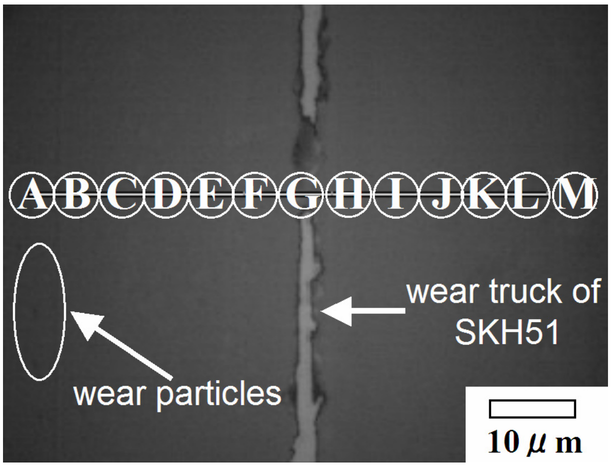


Fig.4 Optical image of the DLC films after sliding 30000 revolutions

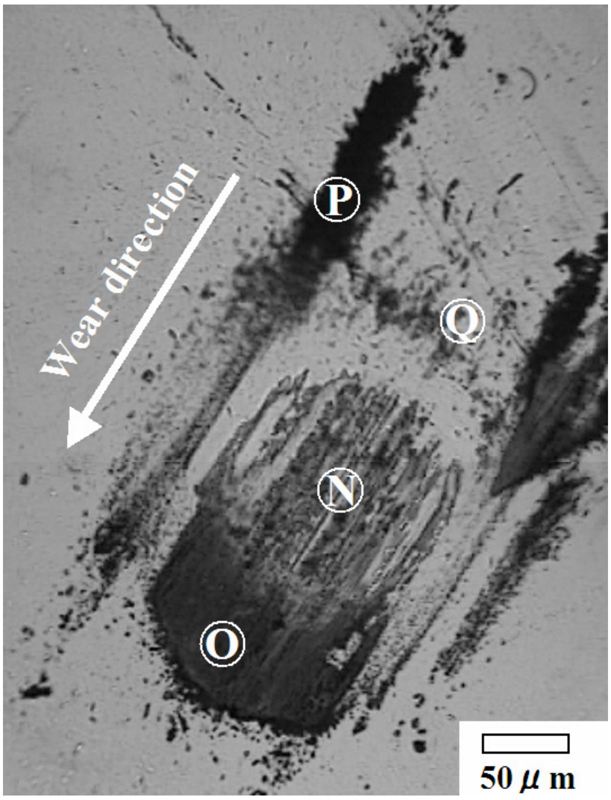


Fig.5 Optical image of the ball indenter surface after sliding 30000 revolutions

thickness and indentation hardness of the DLC films is 0.37 μm and 17.6 GPa respectively.

A sliding test of the DLC films is accomplished by the ball on disk tester shown in Fig.2. A steel ball, corresponding to JIS SUJ2, with 6 mm diameter is used as the indenter. The applied load, the revolution speed and the radius of revolution are 1.0 N, 100 rpm, and 3 mm (a tangential speed is about 31.4 mm/s) respectively.

In order to analyze the wear process, micro laser

Raman spectroscopy is employed against the worn surface after the sliding test. The incident laser excitation is 532 nm provided by a doubling-YAG laser source. The polarized spectra are recorded in the range of 1000-2000 cm^{-1} of Raman shift with the spectral resolution of less than 2.0 cm^{-1}. The laser spot size is about 5 μm, where the laser power decreased by the filters is 25 μW, and an objective lens with a magnifying power of 100 is used to focus the light on the worn surface.

3. Results

3.1. Sliding test

Fig.3 shows the results of the sliding test as a change in the friction coefficients. The tests for 10000 and 30000 revolutions are compared. From the results, the result of 10000 revolutions lies on the result of 30000 revolutions. The friction coefficients gradually increase in the revolutions at the first stage (~13000 revs.), then the coefficients decrease at the second stage (13000~18000 revs.), and finally the coefficients take approximately constant values at the third stage (18000~30000 revs.). The wear tracks originating from the steel ball indenter contacts with the substrate start to grow at the second stage. Fig.4 shows the optical image of the DLC films after a sliding of 30000 revolutions. The wear tracks on the substrate can be observed clearly. The wear particles can also be observed around the wear tracks. Fig.5 shows the optical image of the wear on the steel ball indenter after a sliding of 30000 revolutions. The hard wear (point N in the figure) and the adhered wear particles (points O and P in the figure) can be observed. In case of 10000 revs., the wear tracks of the substrate and the hard wear of the indenter can not be observed although the adhered wear particles can be observed.

3.2. Micro Laser Raman Spectroscopy

A mapping measurement using micro laser Raman spectroscopy is accomplished against both the wear tracks of the DLC films and the surface of the indenter. The measurement points of the wear tracks and the surface are indicated schematically from the points (A) to (M) in Fig.4 and from the points (N) to (Q) in Fig.5. The mapping step is 5 μm and 30 scans are achieved at each measurement points.

Figs.6 and 7 show the results of the Raman spectra at from (A) to (F) and from (H) to (M). They are typical DLC spectra. Usually the Raman spectra of DLC films are characterized by the G peak around 1550 cm^{-1} and the D shoulder peak around 1350 cm^{-1}. On the other hand, the G peak around 1570 cm^{-1} and the D peak around 1390 cm^{-1} in the spectra shown in Figs.6 and 7 can be observed. These results mean that the DLC films used in this study must be the hydrogenated DLC films because the G and D peaks of a conventional hydrogenated DLC films shift towards a higher wavenumber, which corresponds to the decreased

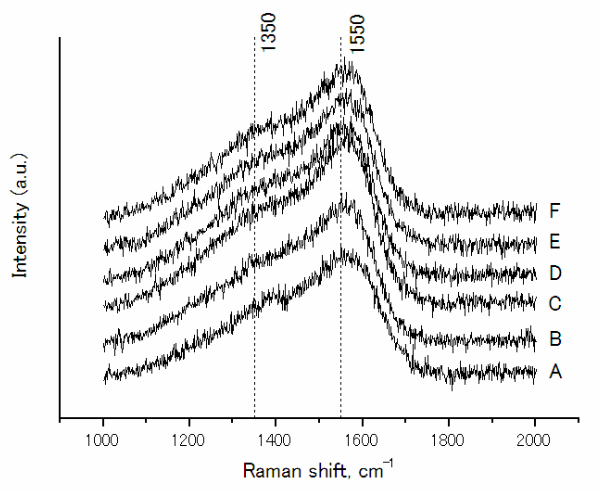


Fig.6 Results of the Raman spectra from (A) to (F)

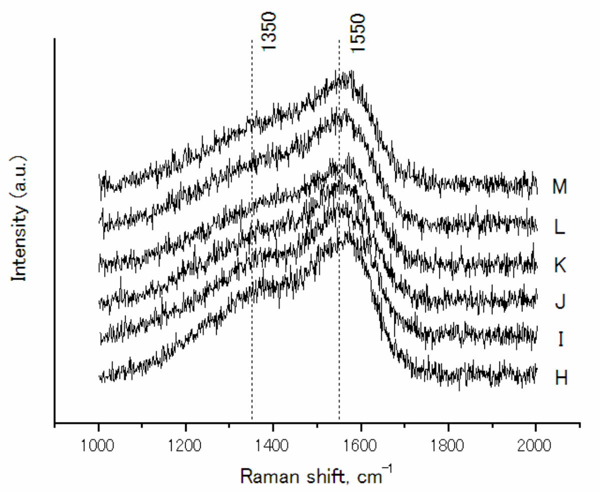


Fig.7 Results of the Raman spectra from (H) to (M)

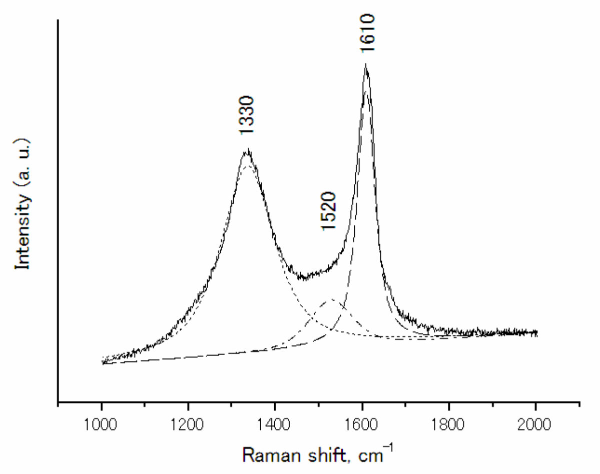
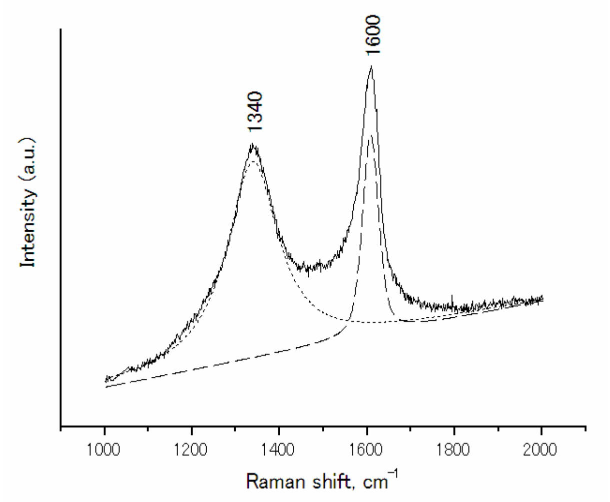
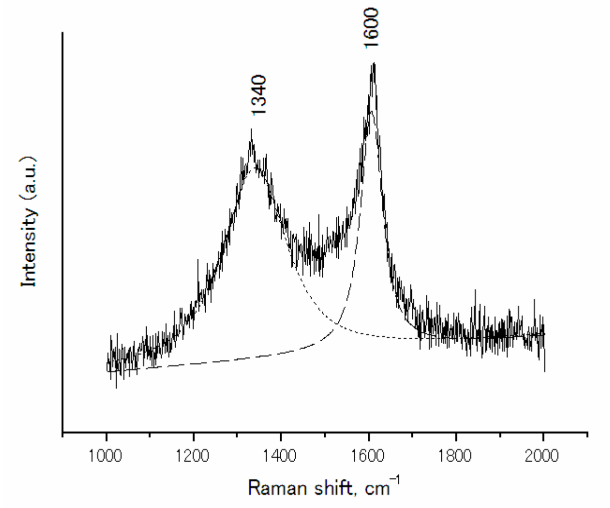


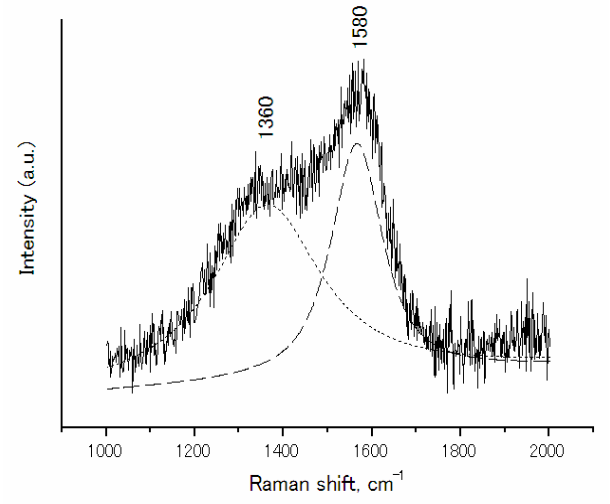
Fig.8 Results of the Raman spectrum at (G)



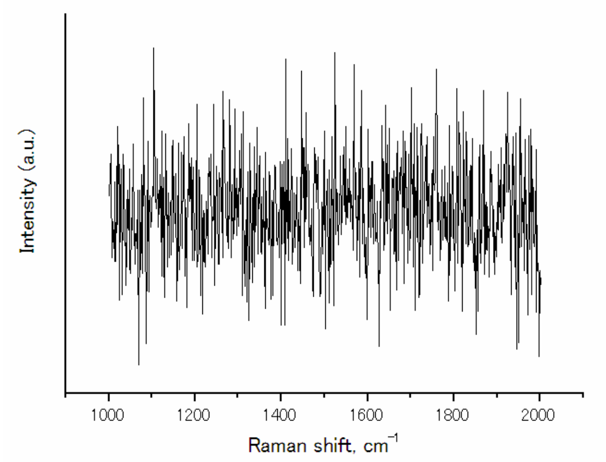
(a) The Raman spectrum at (N)



(b) The Raman spectrum at (O)



(c) The Raman spectrum at (P)



(d) The Raman spectrum at (Q)

Fig.9 Results of the Raman spectra at the surface of the indenter after sliding 30000 revolutions

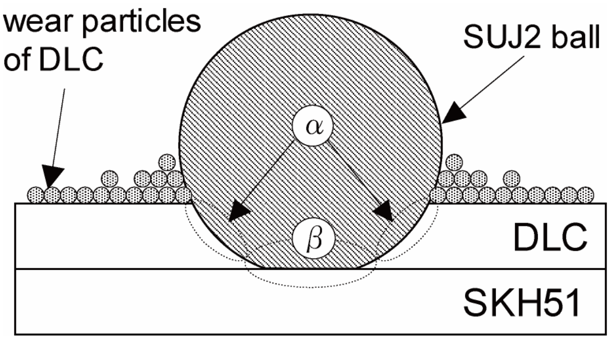


Fig.10 Schematic illustration of the sliding interface

diamond like characteristics of the films[1,12-14]. All of the Raman spectra shown in Figs.6 and 7 are almost same to each other. Consequently, it is possible to consider that there are no changes in the structure of the DLC films due to the sliding. In contrast, obvious changes in the Raman spectrum at (G) peaks are observed as shown in Figs.8. This will be caused by the occurrences originating from the contacts between the substrate and the indenter during the sliding test[15,16].

The Raman spectra at (N) and (O) are shown in Figs.9a and 9b, respectively. Although the detected intensity is different, the shapes of these spectra are almost same as compared to that at (G). This means that each spectrum is coming from the same structure of the subjects. On the other hand, Raman spectrum at (P) shown in Fig.9c is similar to the spectra shown in Figs.6 and 7. Comparing the spectrum at (O) with that at (P) the structure of the wear particles is found to be obviously different to each other, i.e., the particles at (O) are dominantly derived from the contact area between the substrate and the indenter, and from around the contact area, while the particles at (P) are dominantly derived far from the contact area. There are no Raman spectra originating from the carbon connections at (Q) as shown in Fig.9d. Therefore the influence of both the carbon compounds and the solid solutions of carbon and iron in the indenter can be disregarded in the Raman spectra.

4. Discussion

Fig.10 shows the schematic illustration of the sliding interface. During sliding at the third stage (18000~30000 revs.) as shown in Fig.3, it is possible to consider that two contact interface occur, i.e., the interface (α) between the DLC film and the indenter, and the interface (β) between the substrate and the indenter. From Figs.6, 7 and 9c, the structure of the DLC films never changes at the interface (α), even though the shape of the DLC will change from the films to the particles by the sliding. In contrast, obvious changes in the structures shown in Figs.8, 9a and 9b are observed at the interface (β), which are likely to be caused by the contacts between the substrate and the indenter. In order to consider the origins of the obvious changes, two possibilities are discussed as follows in this study.

Compositions of both the substrate and the indenter may be influenced by the sliding that affected the Raman spectra because both the substrate and the indenter include carbon compounds and solid solutions of carbon and iron[17)]. In this study, the sliding tests for the substrate and the indenter without the DLC films are accomplished under the same test conditions described previously. There are no Raman peaks originating from the carbon connections. Consequently, the influence of the change in the structure of both the substrate and the indenter by the sliding in the Raman spectra shown in Figs.8, 9a and 9b can be disregarded.

From Figs.8, 9a and 9b, the Raman spectra will indicate severe degradation of the structural properties of the DLC films. In order to investigate the changes in the structure and the thermal stability of the DLC films, annealing test of the DLC films is accomplished in this study. Fig.11 shows the results of the Raman spectra after this test. The tests annealed for 1 hr are conducted in an atmosphere of oxygen and in vacuum, and are holding for 1 hr. From the figure, the changes in the structure of the DLC films are never observed until 673 K. The change occurs at 973 K (in vacuum), where as in an atmosphere of oxygen the DLC films get decomposed to CO_x gas at 973 K. The Raman spectrum at 973 K in vacuum is similar to that as shown in Fig.8, 9a and 9b. Generally, the Raman spectra of the hydrogenated DLC films is composed of two broad band, disordered aromatic (D shoulder peak, ~1350 cm^{-1}) and symmetric stretching mode of graphite (G peak, ~1550 cm^{-1})[1,12-14)]. At high annealing temperature of more than 673 K, the enhanced mobility of atoms may cause the relaxation of compressive stress in the films and the desorption of hydrogen atoms from the films, thus inducing an increase of the order of sp^2-bonded clusters, i.e., graphitization. As a result of the graphitization, the D and G peak curves tend to be separated as distinct peaks are indicative of the more graphite materials[18-20)]. The presence of the separated D and G peaks shown in Figs. 8, 9a, 9b and 12 indicates the graphitization of the DLC films. Since one of the origins which induces the graphitization of the DLC films is high temperature of more than 673 K as mentioned above, it will be possible to consider that the flash temperature and the friction heat at around the contact interface (β) during the sliding as shown in Fig.10 contain the temperature of more than 673 K and the subordinate friction heat[21,22)]. On the other hand, no change in the structures as shown in Figs.6, 7 and 9c means that the flash temperature and the friction heat at the contact interface (α) is less than 673 K. In addition, the friction coefficients at the third stage (Fig.3) being lower than those of the first stage, will be caused by the graphitization of the DLC films.

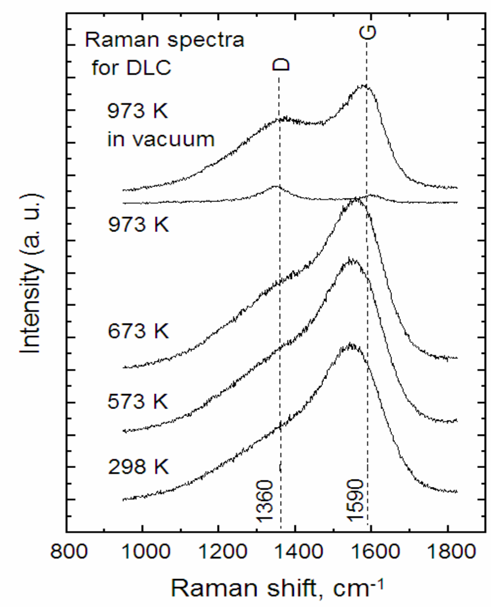


Fig.11 Results of the Raman spectra after annealing

In addition to the friction heat, shearing stress imposed on the DLC films and wear debris are likely to correspond with the transformation of the structure[23)], however, in order to discuss the origin in detail, it is necessary to investigate and analyze the behaviors in the future works.

5. Conclusion

In this study, DLC films are deposited on high-speed tool steel (SKH51) surfaces by PBII&D method. A sliding test of the DLC film is accomplished by the ball on disk tester and then the worn surface is analyzed by micro laser Raman spectroscopy. The results obtained are summarized as follows:

(1) Except for the Raman spectra originating from

around the contact between the substrate and the indenter during the sliding, the Raman spectra from the other areas are almost same and this fact implies no changes in the structure of the DLC film. These mean that the effects of the sliding on the change in the structures can be neglected.

(2) Obvious changes in the structures of the DLC films are observed from the Raman spectra originating from around the contacts between the substrate and the indenter. This will be caused by the graphitization of the DLC films during the sliding.

(3) The carbon compounds and the solid solutions of carbon and iron included in the substrate and the indenter hardly influence the Raman spectra with or without the sliding.

From the above results the relations between the change in the friction coefficients and the change in the structures of the DLC films are identified and have been estimated in this study.

6. References

[1] Robertson, J., “Diamond-Like Amorphous Carbon,” Mater. Sci. Eng., R 37, 2002, 129-281.

[2] Donnet, C., “Recent Progress on the Tribology of Doped Diamond-Like and Carbon Alloy Coatings: A Review,” Surf. Coat. Techn., 100-101, 1998, 180-186.

[3] Grill, A., “Diamond-Like Carbon: State of the Art,” Diam. Rel. Mater., 8, 1999, 428-434.

[4] Grill, A., “Electrical and Optical Properties of Diamond-Like Carbon,” Thin Solid Films, 355-356, 1999, 189-193.

[5] Erdemir, A., “The Role of Hydrogen in Tribological Properties of Diamond-Like Carbon Films,” Surf. Coat. Techn., 146-147, 2001, 292-297.

[6] Grill, A. and Patel, V., “Tribological Properties of Diamond-Like Carbon and Related Materials,” Diam. Rel. Mater., 2, 1993, 597-605.

[7] Donnet, C. and Grill, A., “Friction Control of Diamond-Like Carbon Coatings,” Surf. Coat. Techn., 94-95, 1997, 456-462.

[8] Liu, Y., Erdemir, A. and Meletis, E. I., “Influence of Environmental Parameters on the Frictional Behavior of DLC Coatings,” Surf. Coat. Techn., 94-95, 1997, 463-468.

[9] Suzuki, M., Ohana, T. and Tanaka, A., “Tribological Properties of DLC Films with Different Hydrogen Contents in Water Environment,” Diam. Rel. Mater., 13, 2004, 2216-2220.

[10] Mitsuo, A., Uchida, S., Morikawa, K., Kawaguchi, M., Shiotani, K. and Suzuki, H., “Effect of Deposition Parameter on Hardness of Amorphous Carbon Film Prepared by Plasma Immersion Ion Implantation Using C_2H_2,” Nucl. Instr. Meth. B, 257, 2007, 753-757.

[11] Nishimura, Y., Chayahara, A., Horino, Y. and Yatsuzuka, M., “A New PBIID Processing System Supllying RF and HV Pulses through a Single Feed-through,” Surf. Coat. Techn., 156, 2002, 50-53.

[12] Li, H., Xu, T., Wang, C., Chen, J., Zhou, H. and Liu, H., “Annealing Effect on the Structure, Mechanical and Tribological Properties of Hydrogenated Diamond-Like Carbon Films,” Thin Solid Films, 515, 2006, 2153-2160.

[13] Santos, L. V., Trava-Airoldi, V. J., Corat, E. J., Iha, K., Massi, M., Prioli, R. and Landers, R., “Friction Coefficient Measurements by LFM on DLC Films as Function of Sputtering Deposition Parameters,” Diam. Rel. Mater., 11, 2002, 1135-1138.

[14] Guerino, M., Massi, M., Maciel, H. S., Otani, C., Mansano, R. D., Verdonck, P. and Libardi, J., “The Influence of Nitrogen on the Dielectric Constant and Surface Hardness in Diamond-Like Carbon (DLC) Films,” Diam. Rel. Mater., 13, 2004, 316-319.

[15] Liu, Y., Erdemir, A., Meletis, E. I., “A Study of the Wear Mechanism of Diamond-Like Carbon Films,” Surf. Coat. Techn., 82, 1996, 48-56.

[16] Scachez-Lopez, J. C., Erdemir, A., Donnet, C., Rojas, T. C., “Friction-Induced Structural Transformations of Diamondlike Carbon Coatings under Various Atmospheres,” Surf. Coat. Techn., 163-164, 2003, 444-450.

[17] “JIS Handbooks, Steel 1,” Japanese Standards Association, 2002, 859 and 912.

[18] Kalin, M., Roman, E. and Vizintin, J., “The Effect of Temperature on the Tribological Mechanisms and Reactivity of Hydrogenated, Amorphous Diamond-Like Carbon Coatings under Oil-Lubricated Conditions,” Thin Solid Films, 515, 2007, 3644-3652.

[19] Bogdanovich, P. N. and Tkachuk, D. V., “Temperature Distribution over Contact Area and “Hot Spots” in Rubbing Solid Contact,” Trib. Int., 39, 2006, 1355-1360.

[20] Cheng, C. L., Chia, C. T., Chiu, C. C. and Lin, I. N., “Time-Dependent in-Situ Raman Observation of Atomic Hydrogen Etching on Diamond-Like Carbon Films,” Diam. Rel. Mater., 11, 2002, 262-267.

[21] Abdel-Aal, H. A., “A Remark on the Flash Temperature Theory,” Int. Comm. Heat Transfer, 24, 2, 1997, 241-250.

[22] Kuhlmann-Wilsdorf, D., “Flash Temperatures Due to Friction and Joule Heat at Asperity Contacts,” Wear, 105, 1985, 187-198.

[23] Zhou, Z. F., Li, K. Y., Bello, I., Lee, C. S. and Lee, S. T., “Study of Tribological Performance of ECR-CVD Diamond-Like Carbon Coatings on Steel Substrates Part 2. The Analysis of Wear Mechanism,” Wear, 258, 2005, 1589-1599.