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Tribochemical Interactions of Si-doped DLC Film Against Steel in Sliding Contact

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Abstract

This study concerns the effects of tribochemical interactions at the interface of Si-DLC (silicon-doped diamond-like carbon) film and steel ball in sliding contact on tribological properties of the film. The Si-DLC film was over-coated on pure DLC coating by radio frequency plasma-assisted chemical vapor deposition (r.f. PACVD) with different Si concentration. Friction tests against steel ball using a reciprocating type tribotester were performed in ambient environment. X-Ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) were used to study the chemical characteristics and elemental composition of the films and mating balls after tests. Results showed a dark-gray film consisting of carbon, oxygen and silicon on the worn steel ball surface with different thickness. On the contrary, such film was not observed on the surface of the ball slid against pure DLC coating. The oxidation of Si-DLC surface and steel ball was also found at particular regions of contact area. This demonstrates that tribochemical interactions occurred at the contact area of Si-DLC and steel ball during sliding to form a tribofilm (so called transfer film) on the ball specimen. While the pure DLC coating exhibited high coefficient of friction (~0.06), the Si-DLC film showed a significant lower coefficient of friction (~0.022) with the presence of tribofilm on mating ball surface. However, the Si-DLC film possesses a very high wear rate in comparison with the pure DLC. It was found that the tribochemical interactions strongly affected tribological properties of the Si-DLC film in sliding against steel.

Keywords: Friction; Wear; DLC; Si-DLC; Tribochemical interactions; Tribofilm

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1. Introduction

In the past decade, diamond-like carbon (DLC) coating has been successfully applied for a wide range of tribological applications as surface protective layers due to the high hardness, low friction and superior wear resistance. Recently, many studies have been conducted to improve properties of DLC film. Nitrogen, silicon and other metals such as titanium, tungsten were introduced into the film to enhance its mechanical and tribological properties (Neidhardt et al., 2004; Wang et al., 2006; Singh et al., 2006; Ouyang et al., 2005). Amongst them, Si-doped DLC (Si-DLC) coating has been considerably attractive as it shows many advantages such as low friction coefficient and better mechanical properties (Oguri et al., 1991; Kim et al., 1999; Lee et al., 1997; Wu et al., 1998). The effects of silicon incorporated component on tribological properties of DLC film in various environments were previously investigated (Wu et al., 1998; Zhao et al., 2001; Ohana et al., 2004).

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Generally, Si-DLC coating exhibits very low friction coefficient, one third that of DLC without doped silicon, in ambient environment where most practical applications are usually employed.

Tribochemical interactions, simply defined as chemical reactions under dynamic tribo-process, were suggested to play a very important role in friction and wear properties of materials (Gogotsi et al., 1992; Nakayama et al., 2006). However, a few studies have dealt with the tribochemical process which occurs at the interface of Si-DLC coating and counter-body in sliding contact. In the literature, just the formation of silicon oxide or silicon-rich oxidized debris when Si-DLC slid against steel ball was earlier reported as contributing to the low and stable friction of the coating (Oguri et al., 1991; Yang et al., 2002).

This work focuses on tribochemical behaviors of Si-DLC film in sliding contact against steel ball in ambient environment. XPS and AES surface analyses were performed to investigate chemical characteristics and composition of both film and steel ball before and after tribotests. The friction and wear properties of Si-DLC films were examined and discussed in terms of the effect of tribochemcal interactions that occurred during sliding in comparison with the pure DLC.

2. Experimental details

2.1 Coating preparation

The DLC coatings in this study were fabricated by r.f. PACVD deposition technique. A DLC layer was first deposited on Si (100) substrate using benzene (C_6H_6) as precursor gas; the Si-DLC film was then over-coated by introducing silane (SiH_4) into coating chamber without breaking the deposition process. Bias voltage and deposition pressure were about – 400 V and 1.33 Pa, respectively. The thickness of the DLC and Si-DLC films controlled by adjusting the deposition time was 2 μm and 0.5 μm, respectively. Silicon concentration of Si-DLC film was varied from 3% to 5% by changing the flow rate of silane component of the gas. Details of the coating process were reported elsewhere (Lee et al., 1997). The coating thickness of 2 μm for the pure DLC and 2.5 μm for Si-DLC/DLC was measured by alpha-step profilometer (Tencor P-1).

2.2 Tribological measurements

Friction and wear tests employing a home-built ball-on-plate type reciprocating tribotester were performed in ambient environment without lubrication. The counter specimen was a bearing steel ball of 3 mm in diameter. Relative humidity was maintained at 42± 5% during the test at room temperature. Prior to the tests, ball specimens were cleaned by using hexane and acetone solvents to remove surface contaminants. The cleaning process is described in detail elsewhere (Pham et al., 2005). The ball was mounted in a carrier head and reciprocated against a flat DLC film. All the tests were performed at an applied load of 1.8N while sliding speed and stroke length was 4.43 mm/s and 3 mm, respectively. Each test was repeated at least three times to check the reproducibility of the friction behavior.

2.3 Characterization of worn surfaces

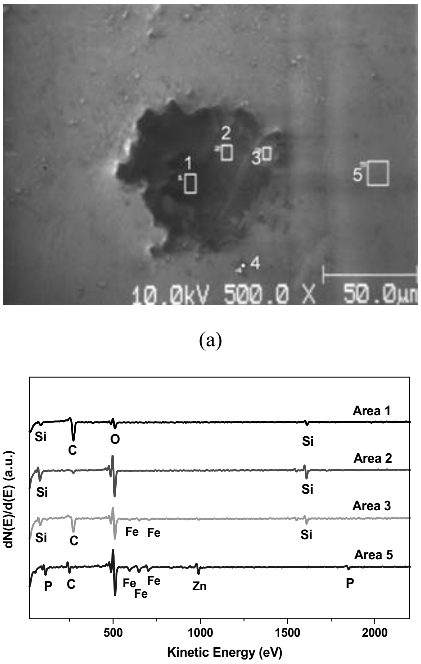
XPS and AES analyses were performed to examine the changes in chemical characteristics and elemental composition, induced by tribochemical interactions during sliding of steel ball on Si-DLC film before and after the tests. AES surface analysis was carried out using a Perkin-Elmer PHI-670 system. The accelerating voltage of emission and the current was 10 kV and 0.0280 μA, respectively. To characterize chemical bonding states of carbon atom in Si-DLC film, the original and worn surfaces were studied by XPS analysis using a PHI-5800 ESCA system. Working conditions were shown in detail elsewhere (Pham et al., 2005). Binding energies were corrected by indexing the C1s peak to its characteristic level of 284.6 eV.

3. Results and discussion

3.1 Tribochemical interactions and the formation of tribofilm

Figure 1 shows (a) scanning electron microscope image (SEM) and (b) physical elemental characterization of worn surface of the steel ball slid against Si-DLC film. The number of sliding cycles was 2,000. By observation, the contact area of the ball seems to be covered by a dark-grey film with different thickness. AES linescan analysis for this area [Fig. 1(b)] just detected small amount of iron at the place (area #3) which likely shows a thin layer of the film, while no iron was found in the central regions (area #1 and #2). A comparison with the original one (area #5) confirms that the ball surface was not exposed at the contact area. However, the analysis results of those selected areas also indicated that the composition and chemical structure were very different from them. Area #1 possesses elemental composition consisting of silicon, carbon and oxygen which is similar to that of Si-DLC. The rich-carbon layer there initially demonstrates the material transfer from coating to the steel ball at this region. At area #2 silicon and oxygen are mainly detected while carbon is very small. Its composition and chemical structure as determined by AES and XPS analyses revealed silicon oxide (possibly SiO_2) and carbon in graphite structure. In region #3 the presence of iron is due to the oxidation of ball surface and tribochemical reaction of iron with carbon atom in air at the tribotest. Elemental composition of this region consists of silicon, carbon, oxygen and iron elements that are assigned to an Fe-C-O-Si system including iron oxide (Fe-O), silicon oxide (Si-O), and possibly a trace of iron carbide (Fe-C).

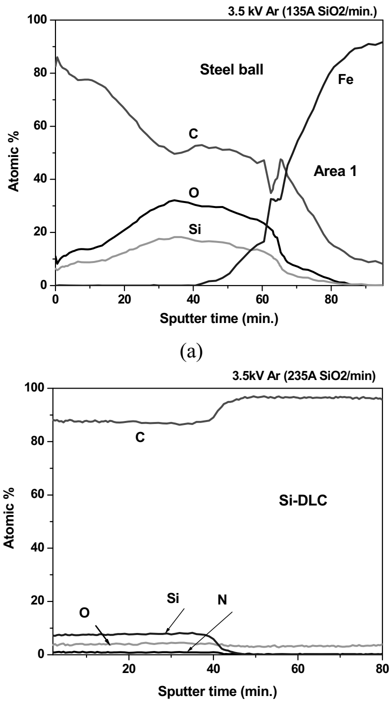
AES depth profile results of different chemical elements for tribofilm (area #1) on worn surface of steel ball and for original Si-DLC coating are shown in Figs. 2(a) and 2(b), respectively. The layer structure of Si-DLC/DLC coating is clearly observed. The presence of silicon for about 40 minutes of sputtering confirms the Si-DLC layer, and then the DLC is below. In case of the ball, a carbon-rich layer is observed until ~30 minutes of sputtering, demonstrating the domination of material transfer of Si-DLC coating at this depth (sputter rate was 135 Å/min. when calibrated against SiO_2). Further depth profiling has observed an underneath layer that consists of iron- and silicon-based compounds as a consequence of a complex tribochemical process. However, the depth profile results for area #2 (not showed here) indicate the silicon oxide instead of rich-carbon layer as mentioned above. Thus, it could be concluded that the oxidation of Si-DLC film and steel ball surfaces, and the material transfer from the film to the ball specimen happened simultaneously in the sliding process. In the literature, the oxidation of Si-DLC coating under friction against steel was also reported to form silicon-rich oxide debris which contributed to the decrease in friction of the film (Oguri et al., 1991; Yang et al., 2002). Furthermore, Gogotsi et al. revealed



(a)

(b)

Fig. 1. (a) SEM image and (b) AES analytical results of worn surface of the ball slid against Si-DLC film after 2,000 sliding cycles. (marked boxes denoted selected regions for AES analysis)



(a)

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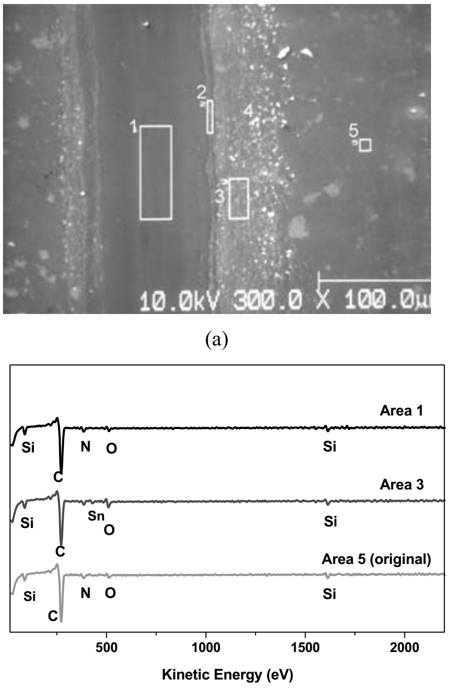
Fig. 2. (a) AES depth profile result for area #1 of steel ball of Fig. 1 and (b) AES depth profile result for original Si-DLC coating.

the oxidation of both ceramic and steel surf-aces during sliding contact in air (Gogotsi et al, 1992). That means oxidation is one of main chemical reactions that happen in the tribochemical process.

For the Si-DLC, AES and XPS analyses were performed in order to investigate elemental composition and chemical structure of the film before and after friction tests. The track made by the test of 6,800 sliding cycles exhibits no complete wear of film surface, although the film is seriously damaged [Fig. 3(a)]. AES analysis results [Fig. 3(b)] for the region inside wear track (area #1) showed elemental composition similar to that of the original (area #5). However, XPS analysis was used since it is difficult to observe the change in chemical structure of the film by AES technique. Figure 4 shows deconvolution C1s peak of (a) original and (b) worn surface after 6,800 cycles of Si-DLC film. In both cases, the XPS spectra of C1s are composed of four components located at 284.1, 284.6, 285.6, and 287.6±0.2 eV which correspond to C-Si, C=C (graphite-like), C-C (diamond-like), and C-O bonds, respectively (Zhao et al., 2001; Paik et al., 2005; Moulder et al., 1995). However, we observed an increase of C=C (sp2 bonding) signal in the chemical structure of the worn surface of Si-DLC in comparison with the original one. This means that the carbon atom in graphitic phase in the top layer of the worn surface of Si-DLC film was increased during the sliding process. On the contrary, at the same time, the C-Si component was reduced in C1s spectrum of the worn surface. From AES results, the decrease of C-Si component is reasonable and can be explained by the decomposition of silicon and carbon atoms under effects of tribochemical process, in which silicon reacted with oxygen in air to form SiO_2 on steel surface.

Therefore, it is confirmed that the tribochemical interactions are evidently observed at contact surfaces of both Si-DLC film and steel ball during friction test and contributed to form a tribofilm on ball surface. It was complex process including the decomposition of silicon and carbon atoms of Si-DLC film, the oxidation of both the film and the mating ball, and the transfer of material from coating to the steel ball surface.

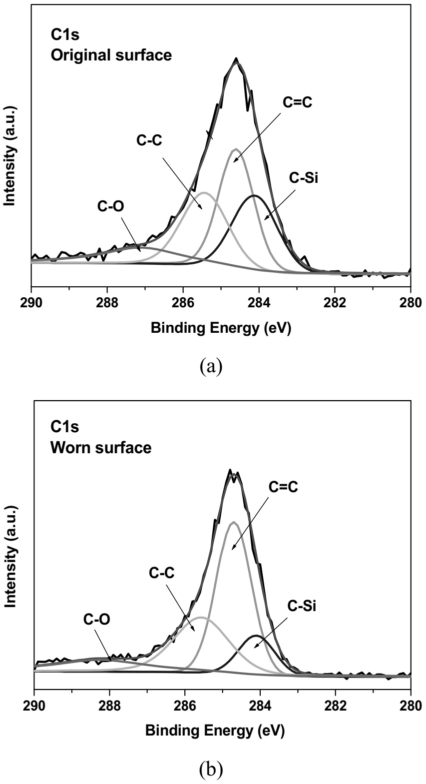
In comparison, a friction test was performed for



(a)

(b)

Fig. 3 (a) SEM image and (b) AES results for selected regions of worn surface of Si-DLC film after friction test of 6,800 sliding cycles.



(a)

(b)

Fig. 4 XPS C1s spectra obtained at (a) original and (b) worn surfaces of Si-DLC film showed in Fig. 3.

pure DLC coating with the same condition. Figure 5 displays the scanning electron micrograph of the worn surface of the ball specimen after 20,000 sliding cycles. The marked boxes indicate selected regions for AES analysis. As shown in this figure, wear scar is clearly observed, although small. Following AES analysis results (not shown here), the elemental composition at the central region of the wear scar (marked as area #1) is dominated by iron, demonstrating that the ball was worn out at this region and iron was exposed entirely. Areas #2, #3, and #4, outside of the scar, showed elemental composition similar to that of original (area #5). The oxidation of the steel surface is also observed at area #1 in the AES results; however, no trace of such a transfer film is observed on the worn surface of the ball (Fig. 5).

3.2 Effects of tribochemical reactions on friction and wear properties of Si-DLC film

Typical friction curves of DLC and Si-DLC film in sliding contact with steel ball are shown in Fig. 6. The Si-DLC film exhibits remarkably lower friction coefficient (~0.022) in the steady state, one third of that of pure DLC. This low friction of Si-DLC could be explained as due to the presence of tribofilm, which mainly consisted of SiO_2 and carbon-rich layer, on steel surface. Furthermore, the increase of graphitic carbon (sp2 bonding) at worn surface of Si-DLC owing to tribo-process also contributed to the reduction in friction of the coating.

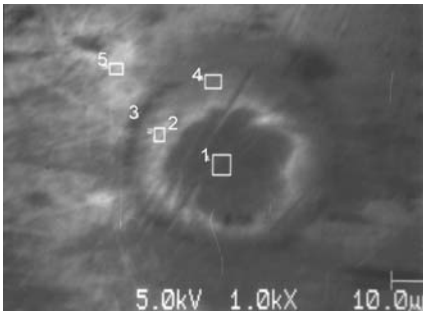


Fig. 5. SEM image of worn surface of the ball slid against pure DLC after 20,000 sliding cycles.

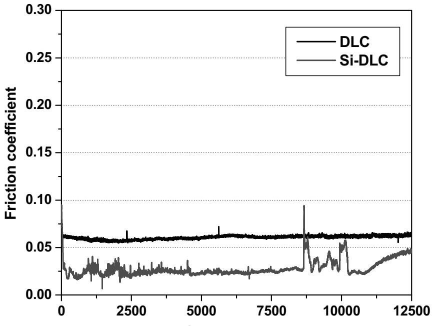
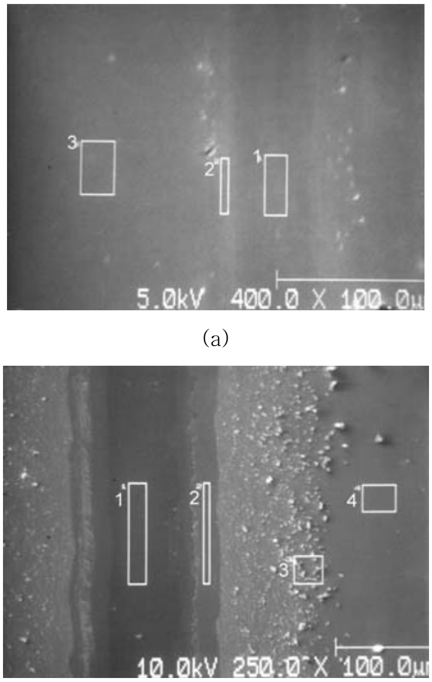


Fig. 6. Friction behaviors of DLC and Si-DLC films in sliding contact against steel ball.

Interestingly, the Si-DLC shows high initial coefficient of friction for several tens of sliding cycles before attaining a low and stable value. It was due to stiction and the gradual formation of the tribofilm as consequence of tribochemical interactions. When the tribochemical process and tribofilm reach steady state, the friction is low and stable. This process happened between several tens to hundreds of sliding cycles in the beginning of our experiments. The unstable and high friction of Si-DLC after ~8700 cycles shown in Fig. 6 could be explained by the break-in process and the partial removal of tribofilm on mating ball. The cracks in tribofilm observed on the ball surfaces at different test cycles indicate the break-in process of the film during sliding. This film was getting thicker with the increase in sliding and reached a saturation level after a certain number of sliding cycles. At the moment when friction started getting high and unstable, the Si-DLC layer was almost removed. Initially, the film is broken and removed rapidly with sliding and the generated particles led to the high and unstable values of friction. In fact, the friction coefficient increased and reached a steady high value when both tribofilm and Si-DLC layer were removed completely. Material transfer leading to the increase in friction coefficient was suggested (Gogotsi et al., 1992); however, it is very difficult to distinguish the role of both silicon oxide and carbon-rich layer from tribofilm in this study. Therefore, we conclude that the tribofilm in this study obviously plays an important role in the reduction of friction for Si-DLC.

Figure 7 shows SEM images of worn surfaces of DLC and Si-DLC coatings generated after tests of 20,000 and 12,500 sliding cycles, respectively. While Si-DLC film was almost completely removed [Fig. 7(b)] in this case, the DLC was just slightly damaged [Fig. 7(a)] despite undergoing a longer tribotest. More-over, the Si-DLC film showed a much larger amount of material removal than that of the pure DLC after 20,000 sliding cycles (Fig. 8). This demonstrates that the pure DLC coating possesses higher wear resis-tance than Si- DLC in this study. The Si-DLC was worn out easily due to the tribochemical process



(a)

(b)

Fig. 7. SEM images of wear track of (a) DLC after 20,000 and (b) Si-DLC after 12,500 sliding cycles.

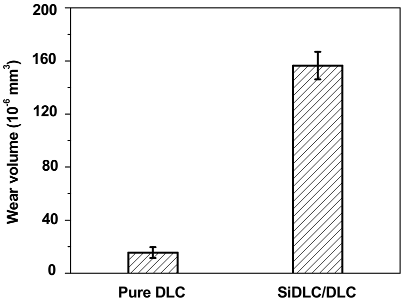


Fig. 8.Worn volumes of the pure DLC and representative Si-DLC/DLC coatings at 20,000 sliding cycles.

that is related to the presence of Si content in the film composition. The wear particles formed contributed to the build up of the tribofilm, which strongly affected the tribological properties of the film as proved above. Therefore, though DLC is harder than Si-DLC, the chemical interactions which were observed in the case of Si-DLC obviously induced the difference in the wear of the films.

4. Conclusions

The tribochemical interaction at the contact surface of the Si-DLC coating slid against steel ball and its effects on tribological properties of the coating were experimentally investigated. The results are summarized as follows:

(1) Tribochemical interactions which occurred at the interface between Si-DLC film and steel ball during sliding contact strongly affected the tribological properties of the film.

(2) Tribochemical reactions including the oxidation of steel ball and Si-DLC film led to the formation of tribofilm that consisted of a carbon-rich layer, Fe-O, Si-O, and Fe-C compounds on ball surface.

(3) The decomposition of silicon and carbon atoms at worn surface of Si-DLC film was identified as due to a triboprocess.

(4) Tribofilm on worn surface of steel ball and graphitic carbon (sp2) which was found increasing on the wear track of Si-DLC film and primarily contributed to the low friction of Si-DLC in sliding contact against steel ball.

(5) Tribochemical interactions induced the higher wear rate of Si-DLC film in comparison with DLC coating.

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References

Gogotsi, Yu. G., Koval'chenko, A. M. and Kossoko, I. A., 1992, "Tribochemical Interactions of Boron Carbides Against steel," *Wear*, Vol. 154, pp. 133~140.

Kim, M. G., Lee, K. R. and Eun, K. Y., 1999, "Tribological Behavior of Silicon-incorporated Diamond-like Carbon Films," *Surface and Coatings Technology*, Vol. 112, pp. 204~209.

Lee, K. R., Kim, M. G., Cho, S. J., Eun, K. Y. and Seong, T. Y., 1997, "Structural Dependence of Mechanical Properties of Si Incorporated Diamond-like Carbon Films Deposited by RF Plasma-assisted Chemical Vapor Deposition," *Thin Solid Films*, Vol. 308~309, pp. 263~267.

Moulder, J. F., Stickle, W. F., Spbol, P. E. and Bomben, K. D., 1995, "Handbook of X-Ray Photoelectron Spectroscopy," *Physical Electronics Inc.*

Nakayama, K. and Martin, J. M., 2006, "Tribochemical Reactions at and in the Vicinity of a Sliding Contact," *Wear*, Vol. 261, pp. 235~240.

Neidhardt, J., Hultman, L., Broitman, E., Scharf, T. W. and Singer, I. L., 2004, "Structural, Mechanical and Tribological Behavior of Fullerene-like and Amorphous Carbon Nitride Coatings," *Diamond and Related Materials*, Vol. 13, pp. 1882~1888.

Oguri, K. and Arai, T., 1991, "Tribological Properties and Characterization of Diamond-like Carbon Coatings with Silicon Prepared by Plasma-assisted Chemical Vapor Deposition," *Surface and Coatings Technology*, Vol. 47, pp. 710~721.

Ohana, T., Nakamura, T., Suzuki, M., Tanaka, A. and Koga, Y., 2004, "Tribological Properties and Characterization of DLC Films Deposited by Pulsed Bias CVD," *Diamond and Related Materials*, Vol. 13, pp. 1500~1504.

Ouyang, J. H. and Sasaki, S., 2005, "Friction and Wear Characteristics of a Ti-containing Diamond-like Carbon Coating with an SRV Tester at High Contact Load and Elevated Temperature," *Surface and Coatings Technology,* Vol. 195, pp. 233~244.

Paik, N. W., 2005, "Raman and XPS Studies of DLC Films Prepared by Magnetron Sputter-type Negative Ion Source," *Surface and Coatings Technology*, Vol. 200, pp. 2170~2174.

Pham, D. C., Ahn, H. S. and Yoon, E. S., 2005, "Friction and Wear Properties of Boron Carbide Coating Under Various Relative Humidity," *KSTLE International*, Vol. 6, No. 2, pp. 39~44.

Singh, V., Palshin, V., Tittsworth, R. C. and Meletis, E. I., 2006, "Local Structure of Composite Cr-containing Diamond-like Carbon Thin Films, " *Carbon*, Vol. 44, pp. 1280~1286.

Wang, A. Y., Lee, K. -R., Ahn, J. P. and Han, J. H., 2006, "Structure and Mechanical Properties of W Incorporated Diamond-like Carbon Films Prepared by a Hybrid Ion Beam Deposition Technique," *Carbon*, Vol. 44, pp. 1826~1832.

Wu, W. J., Pai, T. M. and Hon, M. H., 1998, "Wear Behavior of Silicon-Containing Diamond-Like Carbon Coatings," *Diamond and Related Materials*, Vol, 7, pp. 1478~1484.

Yang, S. H., Kong, H. S., Lee, K. R., Park, S. J. and Kim, D. E., 2002, "Effect of Environment on the Tribological Behavior of Si-incorporated Diamond-like Carbon Films," *Wear*, Vol, 252. pp. 70~79.

Zhao, J. F., Lemoine, P., Liu, Z. H., Quinn, J. P., Maguire, P. and McLaughlin, J. A., 2001, "A Sudy of Microstructure and Nanomechanical Properties of Silicon Incorporated DLC Films Deposited on Silicon Substrates," *Diamond and Related Materials*, Vol. 10, pp. 1070~1075.