Effects of Intermediate Layer in DLC Thin Film on Al_2O_3 for Improvement of High Temperature Strength

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DLC coating on ceramics is very useful for manufacturing the materials with hardness and low friction. Adhesion of DLC thin film on ceramics, on the other hand, is usually very weak. Adhesion of DLC film depends on many parameters such as contamination and chemical bonding between thin film and substrate. In this study, adhesion of DLC film on ceramics was improved by the intermediate layer when the plasma immersion ion deposition (PIID) technique was applied. It is found that the chemical composition and the thickness of intermediate layer have significantly an effect on the adhesion of DLC thin film on Al_2O_3.

Keywords : DLC thin film, Intermediate layer, PIID, Adhesion, Alumina

1. INTRODUCTION

Thin film of Diamond-like-carbon (DLC) is an attractive materials because it has high hardness, inertness and tribological properties, for instance, such as high wear resistance and low friction. It is known that thin films with high contents of sp3 hybridized orbital, which is also called diamond bonding, exhibit high hardness and wear resistance like diamond[1-4]. Various deposition techniques have been developed to synthesize the DLC thin film, including ion-beam deposition, plasma source ion implantation, DC and RF magnetron sputtering, arc-physical vapor deposition(arc-PVD), plasma enhanced chemical vapor deposition (PECVD) and laser ablation[5-9]. DLC films have recently been applied to many industrial fields such as bearing, gear, seal, cutting tool, forming tool and mold parts demanding for wear resistance and low friction. It showed higher potential possibility as thin film materials with wear resistance than other thin films like TiN, TiC, TiAlN and CrN.

Alumina ceramics are widely used in many severe environments such as in corrosive, high temperature and highly loaded situations where polymeric materials are used as the counter part of alumina ceramics in seals application to reduce the ceramic-to-ceramic wear. Therefore it is true that high temperature lubricant is an essential for the application of ceramics in high temperature. Consequently there is a need to improve the surface properties of the ceramic by using surface modification techniques such as the thin film process. For this purpose, the experiment was conducted by a high temperature tribo-tester under temperature ranges between 25~400℃. Furthermore, the wear test specimens were analyzed by SEM with EDS to investigate the worn surfaces and cross section of DLC films.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The Al_2O_3 specimens with 5 mm thickness and 50 mm diameter were prepared by grinding with diamond pad of 1500 grit and polishing with diamond powder of 0.25 ㎛, and, as a final step, the ultrasonic cleaning was performed in acetone and alcohol bath, respectively. The roughness of substrate was obtained as Ra=0.05 ㎛. The specimens were put in vacuum chamber and evacuated to base pressure of 2.67×10^{-4} Pa and then the working gases like Ar, H_2, CH_4, C_2H_2 were injected into vacuum chamber. The flow of gases was controlled using the mass flow controller. The parameter that is applied for each 3 step was as following : RF discharge with pulse voltage of 4 kV, pulse width of 20 ㎲ and process pressure of 15 mTorr.

Prior to the deposition of DLC, ceramic surface was cleaned using the Ar ion bombardment by introducing Ar gas as a source gas with an energy of 3 keV for 1

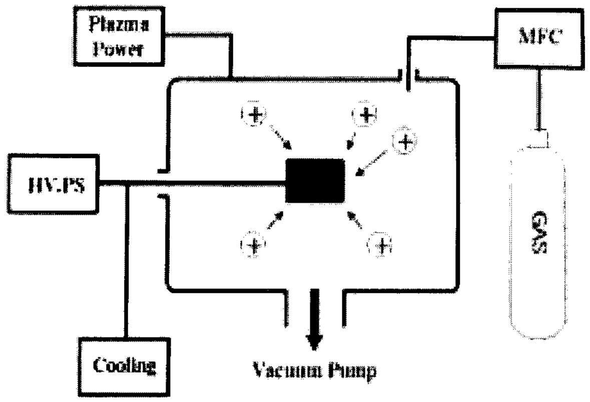


Fig. 1. Schematic diagram of PIID system.

hour at the pressure of 6.6×10^{-2} Pa. DLC films were deposited by using a plasma immersion ion beam deposition (PIID) system as shown in Fig. 1.

As the experimental conditions, PK5 coating condition is Ar sputter cleaning for 1 hour and Si bond layer deposition for 2 hours. DLC coating time is total 7 hours with 2 stages. As 1 stage, the gases are $Ar:H_2:H_4=$ 10:10:10 sccm during the first 4 hours, and as 2 stage, the gases are $C_2H_2:CH_4=$ 65:10 sccm during the last 3 hours. PK6 coating condition is Ar sputter cleaning for 1 hour and Si bond layer deposition for 2 hours. DLC coating time is total 9 hours with 2 stages. As 1 stage, the gases are $Ar:H_2:CH_4=$ 10:10:10 sccm during the first 6 hours, and as 2 stage, the gases are $C_2H_2=$ 65 sccm during the last 3 hours.

The tribological performance for obtained DLC film was evaluated using a high temperature ball-on-disk wear tester to investigate the capabilities as solid lubricant, and 5 temperature conditions were selected from 25～400 ℃. In order to measure the coefficient of friction, friction force was measured through the strain gauge equipped with load cell, and recorded by the data acquisition system consecutively. The 5 mm diameter alumina ball was slid against the coated Al_2O_3 specimen. The applied normal load in tribological test was 2.9 N, which corresponds to initial Herzian stress of 1.3 GPa, and the sliding speed was 0.1 m/s in all tests. Then the wear track was examined using scanning electron microscopy(SEM) with Energy Dispersive Spectroscopy (EDS) in order to investigate the failure mode of DLC solid lubricant.

Scratch tests were conducted using a commercialized scratch tester. A cartridge with a diamond stylus having a radius of 15 ㎛ was swung parallel to the surface of a DLC film sample on X-Y translator with a tilt-table, and moved horizontally, normal to the swing. As the sample moved, the stylus was gradually pressed down upon the sample until the friction force abruptly increased. The

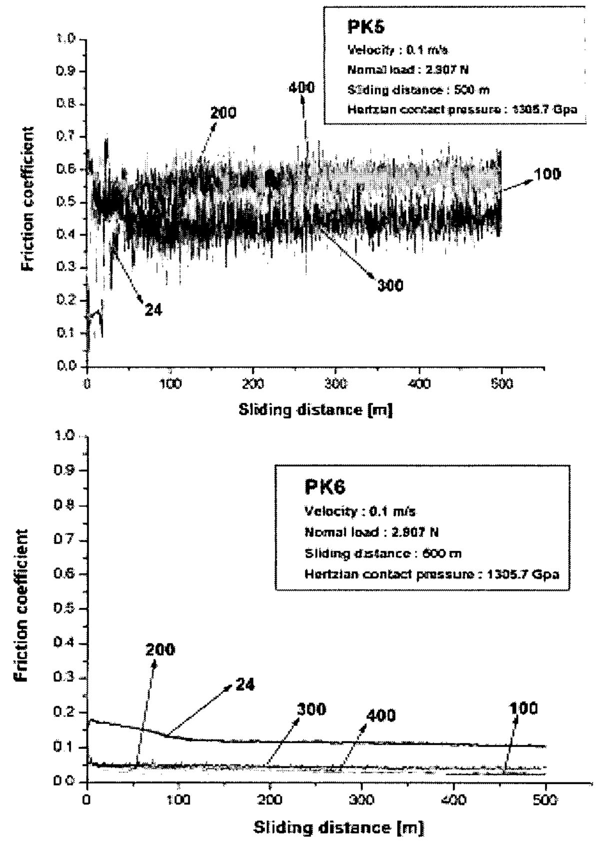


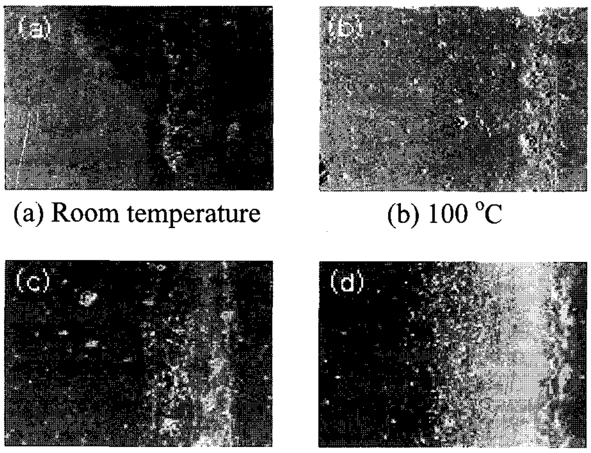
Fig. 2. Friction coefficient of alumina coated with DLC in conditions of PK5 and PK6.

load which lead to the abrupt increase of friction coefficient is defined as the rupture load[10]. Scratch tests were carried out under progressive Load type, 100 N/min loading rate, 10 mm/min speed and about 10 mm scratch length. The effect on the micro-structure change of thin DLC film was analyzed by SEM with EDS.

3. RESULTS AND DISCUSSION

3.1 Tribological test

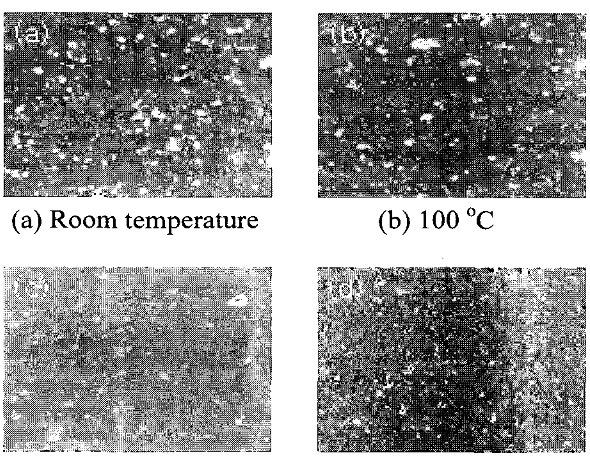
Figure 2 shows the friction coefficients for the DLC coating samples in conditions of PK5 and PK6, respectively. In the case of PK5, which is the condition of room temperature, the friction coefficient is started at about 0.2 and it is increased abruptly, and then stabilized at an average of about 0.6, as observed in figure. A high noise (wide band of friction) is also observed. The case of PK6, on the other hand, shows very low friction coefficient of about 0.08～0.11. An abrupt increase of friction coefficient in pure DLC film indicates that they were completely laminated during the wear test, which means that coating was failed. The coating failure in pure DLC film might result from their lower film



(a) Room temperature (b) 100 °C

(c) 300 °C (b) 400 °C

Fig. 3. SEM photographs of wear track with respect to temperature in condition of PK5.



(a) Room temperature (b) 100 °C

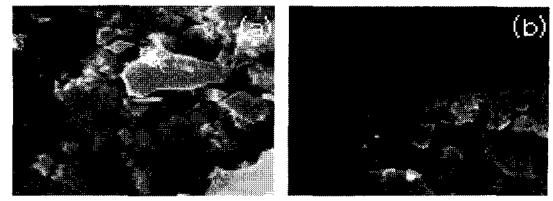
(c) 300 °C (d) 400 °C

Fig. 4. SEM photographs of wear track with respect to temperature in condition of PK6.

thickness and higher hardness value than those of Si containing DLC film[11].

3.2 Wear test

Figure 3 and 4 show the SEM images, which is alumina disc coated with DLC film, of wear track with respect to temperature. In the case of PK6(Fig. 4.), the surface of disc appears relatively clean even though it has a little wear track, and do not exhibit significant damages because wear is almost not occurred. In this case, friction coefficient of DLC coating was measured at less than 0.2. Friction coefficients of DLC films prepared by pulsed bias were approximately in the range of 0.15 ~ 0.25 under high temperature environment.



(a) 200 °C at PK5 (b) 200 °C at PK6

Fig. 5. Two type of fractured DLC film.

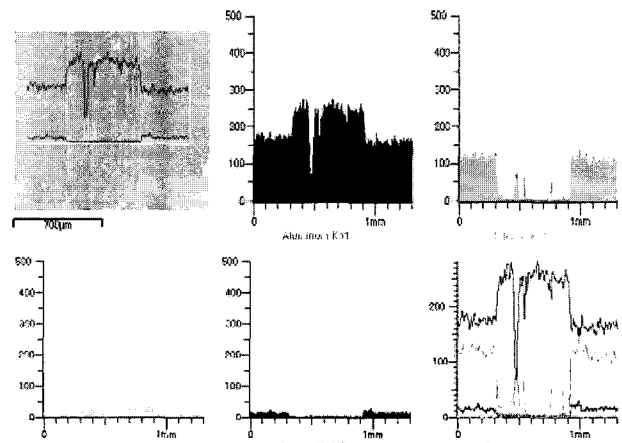


Fig. 6. SEM image and line scanning by EDS analysis of beside wear track after wear test.

However, in the case of PK5(Fig. 3.), many damages are observed during sliding test. DLC film was peeled off and fragmented. According to the deposition conditions, it was found that wear ability of DLC film depends largely on the difference of adherence strength between DLC film and substrate. At a room temperature, DLC film is easily peeled off. Because thick Si layer leads to a fracture of DLC film. In order to improve the adhesion strength of DLC film on substrate, the surface treatment were varied. The relationship between wear rate and hardness of films does not contradict the result reported by Wazumi et al[12]. It revealed that the hard films showed low wear rate in the mild friction condition at load of 2 N. Generally, the increase of film hardness leads to decrease of wear resistance[13].

Figure 5 shows surface appearance in the boundary of fractured DLC coating after performing wear test. In the cases of 200 °C temperature, the boundary of destroyed DLC film is apparently observed with a few debris. However, the boundary of destroyed DLC film has different appearance. The fragment of fractured DLC coating was stretched by sliding alumina ball during wear test. These properties could be only appeared at high temperature over 300 °C. Therefore, the fragment is occurred mainly in the center of wear test track. Another

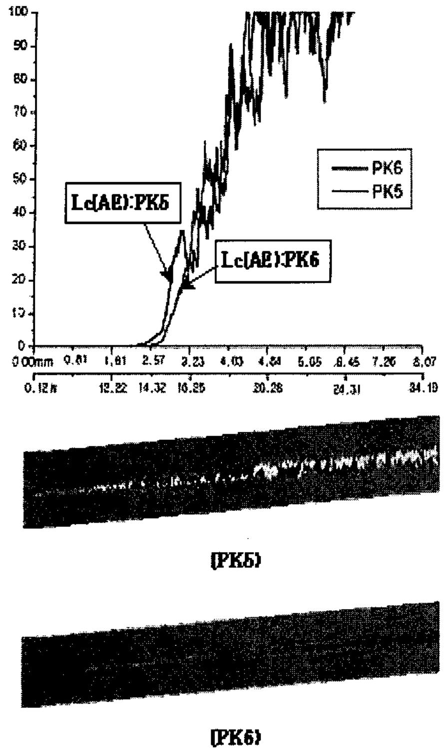


Fig. 7. Steady state acoustic emission of DLC number PK5 and PK6 under 40N load rate with progressive scratch tester.

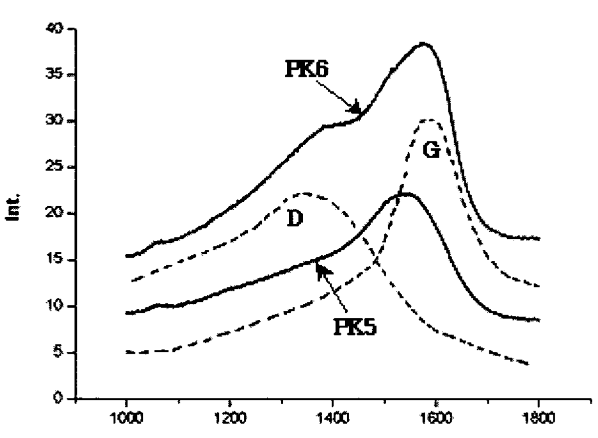
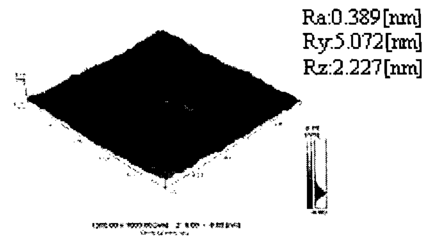


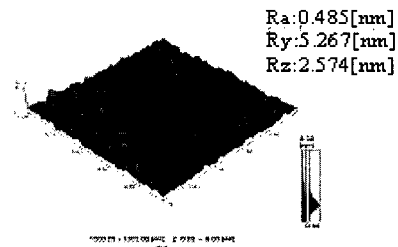
Fig. 8. The Raman spectrum of DLC film.

is type of torn film. Torn film is appeared at side of wear track. In this case, DLC film is subjected to shear stress due to movement of alumina ball along sliding track. lamination is occurred mainly in this area.

Figure 6 show the side of wear track after wear test. Most of the wear debris existed on the outside of the wear track, while there was a small amount of wear debris inside of the wear track. The boundary of the wear track was divided into three zones. In inside of track, DLC films were peeled off completely. There is small amount of wear debris. There is the plastic deformation area developed from alumina hole. In outside of track, DLC film is almost not changed. However, many debris pile up on the DLC film. Debris are mainly consisted of particles of DLC film and alumina. Zone between inside and outside of track was peeled off, however, intermediate material layer still remains. It is not observed the plastic deformation, and just a little debris exist in this zone.



(a) PK5



(b) PK6

Fig. 9. AFM images of surface morphology of DLC film.

3.3 Scratch test

Figure 7 shows a curve of scratch test for the PK5 and PK6. Acoustic emission was recorded with respect to normal load(L). A sharp rising of curve indicates that film failure occurs, which can be considered as a criterion to determine a critical load(Lc). The good adhesion may result from the fact that SiO_2 is chemically more compatible to oxides, due to stability of the SiOx oxides and their mixture with SiO_2 material. The atoms of very thin mixing region between DLC film and SiO_2 region may form a strong covalent bond network, which results in very stronger adhesion than those of DLC film deposited on SiO_2 directly.

3.4 Raman test

Figure 8 shows the Raman spectrum of DLC film on SiO_2 interlayer. The Raman band centering at 1300~1600 cm^{-1} can be decomposed into D peak at 1320cm^{-1} and G peak at 1550 cm^{-1} using Gauss fitting.

The intensity ratio of the G peak to the D peak is 1.6, which is considered to reflect the ratio of C(sp3) to C(sp2) in the DLC film[15-17]. As for these samples, AFM images of the surface morphology are shown in Fig. 9.

A small Rz roughness of 0.22 nm indicates a very smooth surface of the DLC film. It was found that the DLC film deposited on SiO_2 substrate directly was partly laminated due to high residual compressive stress after exposing to air for several days. However, lamination of DLC film was not observed for DLC/SiO_2 structure despite the sample was stored in the air for several months, which means that adhesion of DLC film to the substrate was enhanced due to SiO_2 interlayer.

4. CONCLUSION

An adhesion of DLC film on alumina ceramics is experimentally investigated by using plasma immersion ion deposition(PIID) in order to find the possibility of tribological application. The obtained concluding remarks are summarized as follows.

1. DLC coating can significantly reduce the friction and the wear of alumina if the coating adhesion is sufficiently maintained under high load.

2. Various intermediate layers of Si have been applied prior to the DLC deposition. As the results, the width of wear track was gradually in crease according to increase of temperature.

3. DLC film in condition of PK6 including Si based intermediate layer was greatly destroyed to fragments, and lamination in case of weak adhesion was due to thick intermediate layer.

4. Si is chemically more compatible to oxide because of the stability of SiOx oxide and their mixture with SiO_2 material. The atoms of very thin mixing region between DLC film and SiO_2 region form strong covalent bond network, which means very strong adhesion.

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