A Wear Study of Diamond-like Carbon Film for Total Hip Arthroplasty Applications

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Received 28 Nov 2005; Accepted 31 Oct 2006

Abstract

This study used two different deposit techniques: microwave plasma assisted chemical vapor deposition (MPCVD) and radio frequency magnetron sputter deposition (RFMSD), to deposit diamond- like carbon (DLC) on Co-Cr-Mo alloy head to obtain better wear resistance of total hip arthroplasty. Wear quantity, wear mechanism, wear debris, micro structure, and morphology of the contact surfaces were obtained by the hip simulator, SEM and AFM. The results show that the DLC layer by MPCVD has higher surface roughness, more wear, lower wear resistance, and higher ID/IG ratio in Raman spectroscopy. But the RFMSD sputtered DLC layer has bigger wear debris, larger number of grooves for ultra-high-molecular-weight polyethylene (UHMWPE), and more wear for UHMWPE. As revealed by the results of the observation of the contact surfaces to determine the abrasion loss of UHMWPE, the UHMWPE against a metal femoral head deposited with DLC using MPCVD shows better wear resistance.

Keywords: Diamond-like carbon, UHMWPE, Wear, Total Hip Arthroplasty

Introduction

Due to the change of social life styles and the advancement of medical science, osteoarthritis has become the most common illness among senile diseases. Articulation surfaces show progressive wear and deformation when osteoarthritis becomes worse. While common conservative treatments fail, total joint replacement is the best choice. The function of the artificial joint is to restore smooth articulation between the bones of the joint. Total hip arthroplasty consists of a femoral component with a head and stem and an acetabular component with a metal backing and acetabular cup [1], and most artificial hip joints use a metallic component articulating against ultra-high-molecular-weight polyethylene (UHMWPE). Wear is a common failure mechanism in total joint replacements and at present is considered as a major constraint on design for joint longevity. Thus, how to reduce the generation of wear debris, and thereby achieving a longer life of orthopedic joint prostheses, has been a technological challenge in biomedical engineering.

Several solutions have been proposed to improve wear performance of artificial joints; these include: (1) improving the methods of preservation and disinfection for UHMWPE; (2) ion-implantation on the surface of metal to form a passive film on the surface; however, its nature of shallow penetration is a major setback; (3) to improve in the design of the geometric consistency between the femoral head and the acetabular cup.

Diamond-like carbon (DLC) coatings have been of interest as a protective coating in biomaterials, since clinical studies showed successful results for DLC-coated Artificial Mechanical Heart Valve (AMHV) [2-3]. Some researchers have investigated the wear rate of UHMWPE against DLC-coated stainless steel, and then reported that the DLC coating reduces the wear of the polymer by approximately seven times, and the DLC coating improves the frictional and wear characteristics of DLC coated Ti-6Al-4V sliding against UHMWPE [4-5].

The investigation regarding the wear of biomaterials (DLC coated and un-coated) conducted by Kim et al. [6] showed that the DLC coating dramatically improved the wear performance of Ti and Ti-6Al-4V, and protected the substrates from corrosion and wear. Sheeja et al. [7] have investigated the effect of roughness of substrate surface on the microstructure, sliding life, wear-resistance, coefficient of friction, adhesion and hardness of DLC coatings prepared on Co-Cr-Mo alloy substrates under only one deposition condition (FCVA technique). The results suggest that the film prepared on the smoother surface exhibits better adhesion and relatively higher hardness.

Concerning the investigation of the wear against medical grade UHMWPE, Platon et al. [8] compared the friction and wear on different material couples used for hip prostheses with contact configurations. It showed that DLC coatings, in

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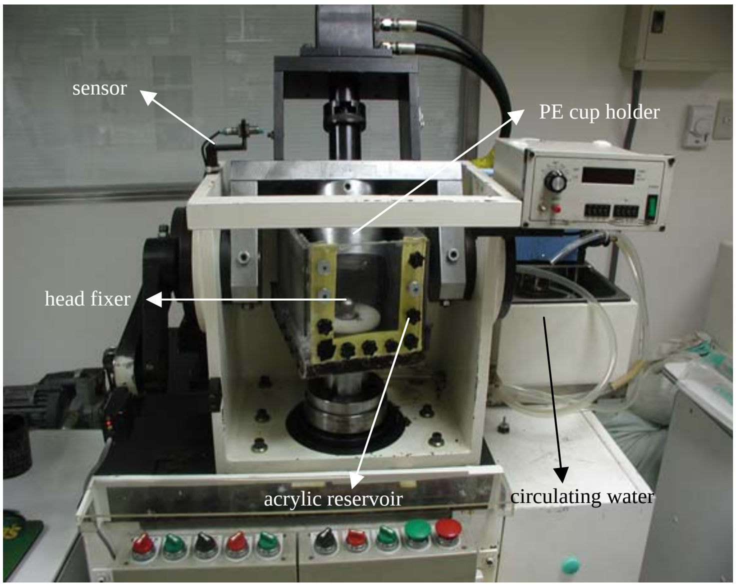

Figure 1. Hip wear testing machine

comparison with UHMWPE, leads to a very low wear rate, approximately equal to an aluminum couple, especially with stainless steel substrate. Tay et al. [9] examined the feasibility of high quality DLC films prepared on Co-Cr-Mo alloy, showed that the wear resistance of DLC coated Co-Cr-Mo alloy against UHMWPE does not show much improvement over uncoated Co-Cr-Mo alloy against UHMWPE. However, the hardness and corrosion resistance of Co-Cr-Mo alloy is increased to a greater extent by DLC coating. Dong et al. [10] used pin-on-disc tribometer to investigate the wear behavior of the tribosystems Ti-6Al-4V / UHMWPE and 316L / UHMWPE in unidirectional sliding motion under the condition of water lubricated, and estimated the wear morphology. They showed that the average wear coefficient of UHMWPE pins against the untreated Ti-6Al-4V disc was about two orders of magnitude higher than that of UHMWPE pins against 316L discs, and Ti-6Al-4V surface could be severely damaged by soft UHMWPE in unidirectional sliding motion under water lubrication. Smith et al. [11] pointed out that the wear rate of UHMWPE was initially higher, and decreased with increasing time.

With respect to the investigating the wear of amorphous diamond (AD) coated biomaterials; Lappalainen et al. [12] showed that in all the combinations, AD coating was able to improve the wear and corrosion resistance compared to uncoated materials.

Recent studies demonstrate that DLC coatings can provide various solutions to the problems of wear and degradation in total joint replacements, and DLC coated stainless steel could show excellent wear resistance; however, the coating is not good at taking concentrated stress and corrosion. Although the principal advantages of titanium alloy (such as Ti-6Al-4V) were thought to have very high biocompatibility, corrosion resistance and excellent mechanical property, but progressive releasing of V and Al ions during the wear process could lead to bad reactions for the human body. However, DLC with its extreme smoothness, hardness, low coefficient of friction, and biocompatibility (DLC is consisting of carbon only), is an excellent candidate for a biomedical alloy / UHMWPE pair to prevent hip joint from ions releasing [13]. In addition, among DLC coatings prepared using many different techniques in aforementioned research, there were no comparisons and conclusions in wear performance and mechanical property of DLC under whole hip joint test condition, and their metallic substrate was usually studied only in disc form.

In this study, the main task is to estimate tribological behavior and mechanical property of microwave plasma assisted chemical vapor deposition (MPCVD) and radio frequency magnetron sputter deposition (RFMSD) DLC coated with Co-Cr-Mo alloy against a medical grade UHMWPE by using hip simulator. The results might be applied for future advanced artificial hip joints applications.

Methods and Experiments

Two femoral heads of 26mm in diameter, from United Orthopedic Corporation were used as the substrate for DLC coatings that were films with a thickness of 0.6 μm produced using MPCVD and RFMSD. Tests were carried out with a hip simulator against four UHMWPE acetabular cups (two used as experiment samples and two used as control samples) obtained from United Orthopedic Corporation. The hip simulator is schematically shown in Figure1.

DLC or amorphous carbon was prepared using RFMSD system and MPCVD with hydrogen, methane, and argon as the reaction gases. Prior to the deposition process of RFMSD, the substrates were ultrasonically cleaned in trichloroethylene, acetone and methanol to remove debris or contaminants, and were dried in nitrogen and loaded into the deposition chamber for RFMSD. In the process of MPCVD, the substrates were ultrasonically cleaned in acetone to remove greasiness and organic matter, and were put in distilled water with diamond powder to increase the density of surface defects in order to increase the adhesion of DLC, and then were dried in acetone and loaded into the deposition chamber for MPCVD.

The hip simulation test was performed with the hip simulator to measure the wear of UHMWPE. One million of cycles were divided into 10 values of loading magnitude per second on the hip joint, which was its loading control. Normal temperature (37℃) of human body was maintained via a cyclic reservoir with constant temperature, in which synovial fluid was simulated using deionized water. The testing results between using synovial fluid and deionized water are almost the same in friction of coefficient, and slightly different in wear of UHMWPE [7]. Hence we used the deionized water to replace the synovial fluid in our experiment. UHMWPE cups were divided into two groups (experiment and control groups). The simulative test was conducted using experiment group at 1.2 Hz for 1 million cycles, and control group was just immersed in deionized water without mechanical load on it. UHMWPE weight was measured individually after the simulative tests, and the amounts of wear were calculated by subtracting the weight of water absorbed by UNMWPE from the weight of wear of UHMWPE. The mechanical characterizations of the films, microstructure, debris and morphology were investigated using Raman spectroscopy, SEM (S-3500N) and AFM (Quesant Q-250). Raman spectroscopy could show that the band position and intensity ratio (I_D/I_G) that could determine the $sp^3/\ sp^2$ bonding ratio and characteristic of its microstructure; the hardness of surface after wear test (DH) were studied by using a Dynamic Ultra Micro Hardness Tester (DUH-W201S, product of Shimadzu).

Results and discussion

3.1 Raman spectroscopy analysis

A typical Raman spectrum of the coatings by MPCVD and RFMSD is shown in Figure 2 and Figure 3, respectively. The test results showed that there were peak bands at 1356.7 cm^{-1} and 1520 cm^{-1}, and the ratio of I_D/I_G was calculated as approximately 0.943 and 0.905 for the DLC coatings by MPCVD and RFMSD, respectively. In general, the D peak and G peak of DLC are often located at about 1360 cm^{-1} and 1550 cm^{-1}. The DLC film was mixed in a mixture of graphite (sp^2) and diamond (sp^3). The increase in I_D/I_G ratio indicates the degree of graphitization of the DLC. As the intensity ratio (I_D/I_G) of the Raman spectra increases, the ratio of the fraction of sp^3 bonds to the fraction of sp^2 bonds decreases. The higher ratio of $sp^3/\ sp^2$ of the coating leads to higher hardness of the present coating. Hence the head coated by RFMS has higher hardness according to the Raman spectroscopy analysis.

3.2 Observations of the surface of DLC coated femoral head before wear

The surface of DLC coated femoral head by MPCVD showed many porous structures (DLC) with very high uniformity above the head (see Figure 4), and the gap between the porous structures and the head substrate was approximately 0.2～1 μm (referring Figure 5). The surface of DLC coated femoral head by RFMSD is shown in Figure 6. The DLC by RFMSD seemed relatively smooth, though with some holes and scratches, which should be caused by the manufacture process.

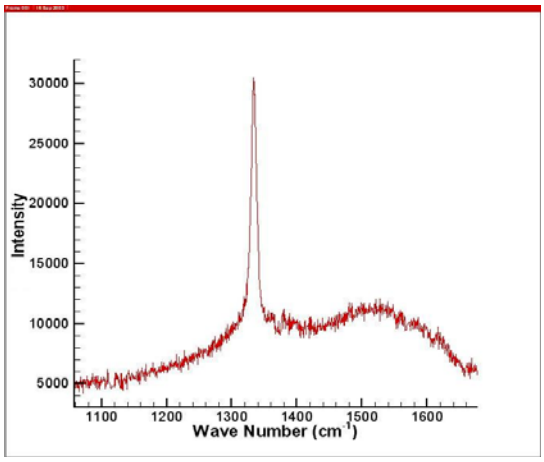

Figure 2. Raman spectrum plot for DLC coated by MPCVD

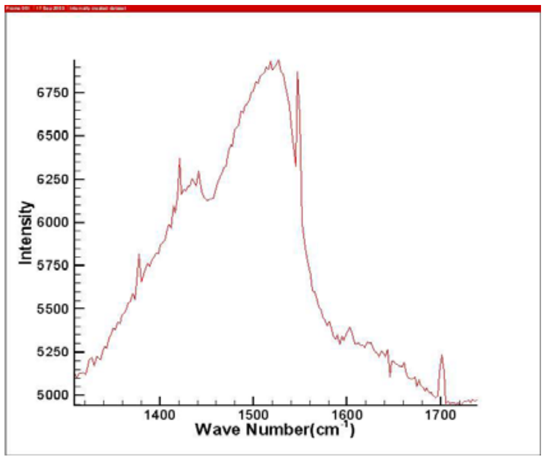

Figure 3. Raman spectrum plot for DLC coated by RFMSD

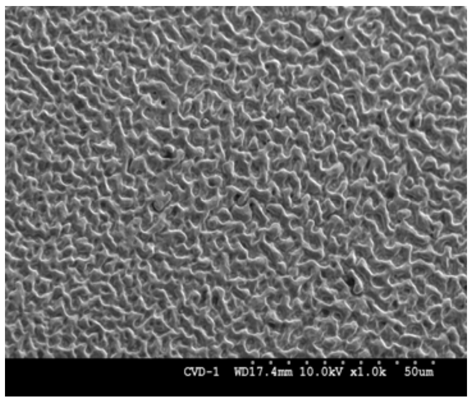

Figure 4. Surface of DLC films on head by MPCVD (1000×)

3.3 Observations of the worn surface of DLC coated femoral head

Figure 7 shows that no porous structure was found, and the major feature of the wear surface of the head coated with DLC by MPCVD was plastic deformation and attachment, which probably indicated that the adhesive mechanism was the

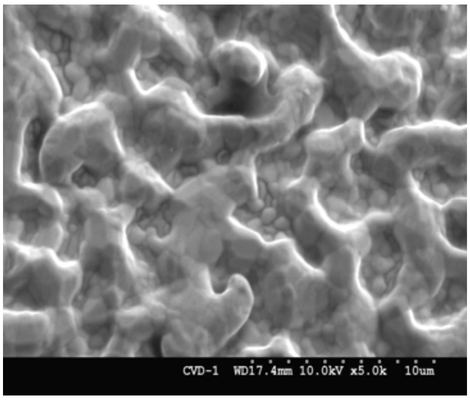

Figure 5. Surface of DLC films on head by MPCVD (5000×)

Figure 6. Surface of DLC films on head by RFMSD (1000×)

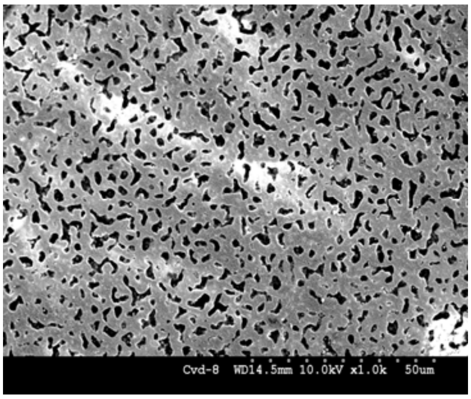

Figure 7. Worn surface of head by MPCVD (1000×)

Figure 8. Worn surface of head by RFMSD (500×)

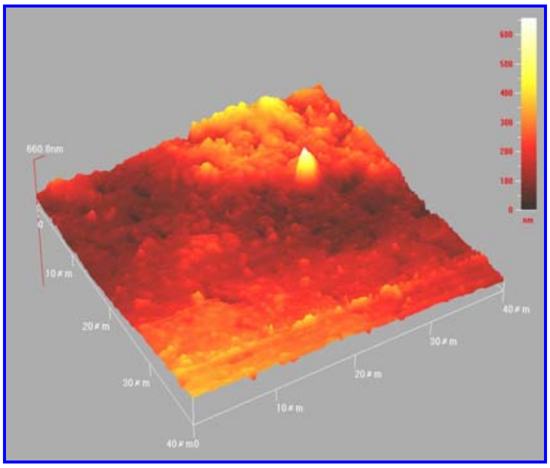

Figure 9. Worn surface morphology of head by MPCVD

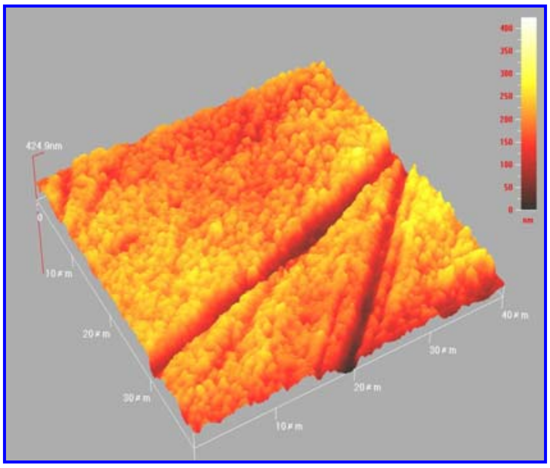

Figure 10. Worn surface morphology of head by RFMSD

dominant wear mechanism. Figure 8 shows that the major features of the wear surface by RFMSD were a large number of scratches, and the generation of debris particles that could cause third-body wear and wear on the contact surface of UHMWPE. These probably indicated that adhesion mixed with some scrape was the dominant wear mechanism of the DLC head coated by RFMSD.

3.4 Wear surface morphology of the femoral head

Some pinholes and grooves near the top of head are shown in Figure 9 (DLC by MPCVD), indicating that the surface of femoral head had slight roughness, approximately 81.96nm in a root mean square (RMS) surface roughness. Figure 10 (for RFMSD) reveals a phenomenon of adhesion and scrape more clearly, indicating that roughness was approximately 42.03nm in a RFMSD surface roughness. By estimating preliminarily the difference between before and after of the wear, the wear was more severe for the surface of DLC coated head by MPCVD than that by RFMSD. So the DLC coated femoral head using MPCVD showed poor wear resistance by considering DLC itself.

3.5 Wear surface hardness of femoral head

The surface hardnesses of the femoral head (DUH (10), the loading is 10 mN) 393.8 and 229.4 were obtained by

Table 1. Results of wear test for UHMWPE cup

	Against MPCVD head		Against RFMSD head	
	Experimental	Control	Experimental	Control
Weight pre-test（g）	12.2796	12.3037	12.3008	12.3037
Weight post-test（g）	12.2829	12.3063	12.1288	12.3063
Weight variation（g）	+ 0.0033	+ 0.0026	- 0.172	+ 0.0026
Weight loss that wear-induced（g）	+ 0.0007		- 0.1746	
Weight loss percentage	+ 5.7005e-3		- 1.419	

Dynamic Ultra Micro Hardness Tester after wear test for DLC coating by MPCVD and RFMSD, respectively. The surface hardness of the uncoated femoral head is 176.5 before wear test. These values indicated that the DLC coated femoral head after wear test is much harder than the uncoated femoral head before wear test.

3.6 Wear test for UHMWPE cup

Table 1 presents the weight losses of the UHMWPE cup measured after 1 million cycles. The percentage of the weight loss of the UHMWPE cup that wore against a DLC coated femoral head using RFMSD was 1.419 %, whereas it rose by 0.0057% approximately for the wear against DLC coated femoral head using MPCVD. Because of the existence of ultrasonic vibration processes, the weight raising phenomenon suggested that there were transfer layers adhered on UHMWPE cup tightly. According to the abrasion loss of cup, two inferences for the case of the cup against head by MPCVD were introduced roughly as follows：

First, for the case of the cup against head by MPCVD, we assumed that lots of transfer layers adhered tightly on the cup inner surface and the weight of the transfer layers was greater than the weight loss that the wear induced.

Secondly, we assumed the weight loss that the wear induced was too little to be neglected for the case of the cup against head by MPCVD, thus the weight gain of the cup was the weight of the transfer layers itself.

But for the case of the cup against head by RFMSD, the weight of the transfer layers was smaller than the weight loss that the wear induced

3.7 Observations of the surface of UHMWPE cup after wear test

Figure 11 (wear of cup against DLC coated head using MPCVD) shows some scratches and grooves, no granular detachment can be found. Figure 12 shows that crisscrossing deep scratches, a severe wear, which probably indicates that scrape mixed with some plastic deformation mechanism was the dominant wear mechanism of the UHMWPE cup against DLC head coated by RFMSD.

3.8 Analysis and observations of the wear debris

Figure 13 (wear of cup against DLC coated head using MPCVD) shows that the wear debris is spindle- and flake-shaped, the size of which is about 4 μm and 1 μm ,

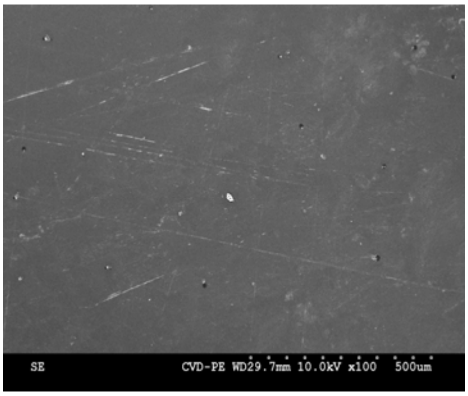

Figure 11. Worn surface of UHMWPE cup (wear against head by MPCVD

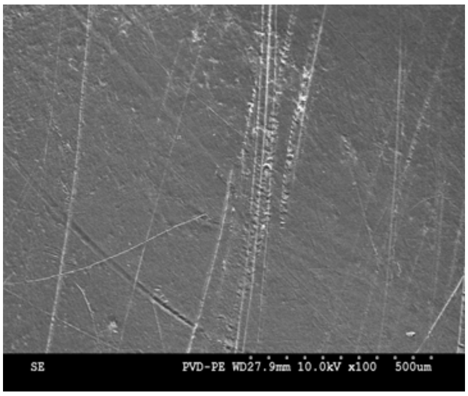

Figure 12. Worn surface of UHMWPE cup (wear against head by RFMSD

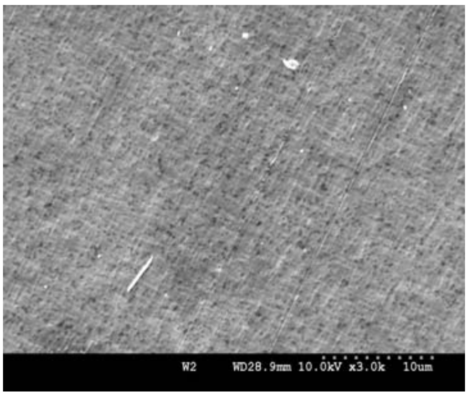

Figure 13. Wear debris for UHMWPE cup / MPCVD head in SEM

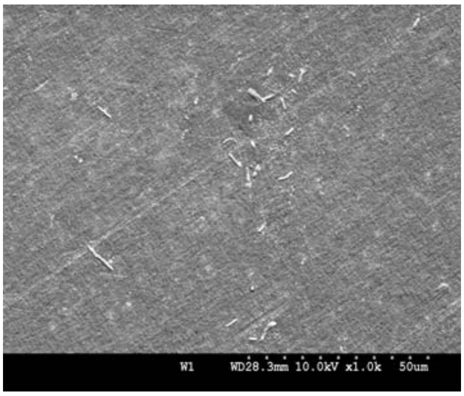

Figure 14. Wear debris for UHMWPE cup / RFMSD head in SEM

respectively. Figure14 (wear of cup against DLC coated head using RFMSD) shows that the main wear debris is spindle-shaped, ranging from 4 to 10 μm . The results suggested that the whole wear debris mainly were spindle- and flake-shaped both for DLC coated head using MPCVD or RFMSD. Because the RFMSD had bigger debris, which could cause severe third-body wear for the couple, and severe wear for UHMWPE.

Discussion

The experimental results show that the UHMWPE against DLC coated head using RFMSD has many scratches on the UHMWPE cup and the femoral head. The UHMWPE cup against DLC coated head using MPCVD has plastic deformation and detachment, probably indicating that adhesion mixed with some plastic deformation mechanism was the dominant wear mechanism.

The UHMWPE against DLC coated head using RFMSD has more and bigger debris than that against DLC coated head using MPCVD, thus causing severe scratches for the surface films on the head and severe wear for UHMWPE as a result. That can explain the phenomenon of scratches was mainly observed for DLC coated head by RFMSD head / UHMWPE cup.

The DLC coated head using MPCVD has higher surface roughness after the wear test than that using RFMSD. The surface of DLC coated head using MPCVD is so easily covered and attached with wear debris that it exhibits relatively higher surface roughness, which is also a reason for less wear debris within the whole pair of DLC coated head using MPCVD / UHMWPE cup.

DLC coated head using RFMSD has low surface roughness difference between that before and after wear test as shown from the surface morphology in AFM (see Figure 10), so we know that it has better wear resistance of head itself. In addition, its amount of wear debris is much more than that head coated using MPCVD, which can easily cause severe wear for UHMWPE, and the generation of wear debris can lead to osteological death of the bone and thus inducing loosening of the joint.

From the view point of wear of UHMWPE cup, the wear of UHMWPE cup against DLC coated head using MPCVD has better wear performance, i.e. little wear debris, small weight loss et al. (see Figure 13 through 14). Hence the UHMWPE together with metal femoral head with deposited DLC using MPCVD shows better wear resistance against UHMWPE cup.

Conclusion

In this study, the main work was to deposit diamond-like carbon on Co-Cr-Mo alloy using two different deposit techniques (MPCVD and RFMSD) to obtain the wear performance of the total hip joint. Wear quantity, wear mechanism, wear debris, micro structure and morphology of the contact surfaces of the aforementioned two couples were studied, and the following conclusions can be drawn from present study：

1. The observations of the surface of the DLC coated head after wear test showed that the adhesion mechanism was used for DLC coated by MPCVD, whereas the adhesion mixed with scrape mechanism was the dominant wear mechanism for DLC coated by RFMSD.
2. The wear of DLC coated head using MPCVD / UHMWPE cup has no granular detachment found for UHMWPE cup, whereas the wear against head using RFMSD showed deep scratches and severe wear for UHMWPE cup.
3. The DLC coated head by MPCVD has higher surface roughness after the wear test, severe wear for the head itself, but has better wear resistance for UHMWPE cup.

Although DLC coated head using MPCVD / UHMWPE cup has severe wear for the head, this pair has better wear performance for UHMWPE cup. Hence from the view point of wear of UHMWPE cup, the UHMWPE cup jointed with metal femoral head deposited DLC using MPCVD might be the best combination of coated alloy head / UHMWPE total hip arthroplasty

Acknowledgement

The National Science Council of R. O. C., Taiwan and the United Orthopedic Corporation financially supported this work under contract No: NSC 92-2622-E-194-007-CC3. This work was also supported by Biomechanics Research Lab. and SEM Lab. of Mackay Memorial Hospital for experimental equipment.

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