Tribological characterization of surface modified UHMWPE against DLC-coated Co–Cr–Mo

D. Sheeja, B.K. Tay, L.N. Nung

Ion Beam Processing Laboratory (Microelectronics Division), School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore-639798

Department of Orthopaedic Surgery, Singapore General Hospital, Outram Road, Singapore-169608

Received 2 August 2003; accepted in revised form 26 February 2004

Available online 17 June 2004

Abstract

The generation of wear particles from the ultra-high molecular weight polyethylene (UHMWPE) counter-face of Co–Cr–Mo/UHMWPE sliding pair is relatively high. These polyethylene wear particles lead to osteolysis and that result in the failure of the implant made with the Co–Cr–Mo/UHMWPE sliding pair. Hence, an investigation has been carried out to enhance the wear resistance of UHMWPE by surface modification of one or either of the sliding surfaces. Tribological characterizations were carried out on good quality diamond-like carbon (DLC) coatings prepared on UHMWPE with and without prior C-ion implantation by filtered cathodic vacuum arc (FCVA) technique in conjunction with high substrate pulse biasing, sliding against uncoated and DLC-coated Co–Cr–Mo.

The evaluations are categorized into two groups: (1) unmodified and DLC-coated UHMWPE with and without prior carbon implantation sliding against uncoated Co–Cr–Mo, (2) DLC-coated UHMWPE with and without prior carbon implantation sliding against DLC-coated Co–Cr–Mo. The study reveals that by coating the UHMWPE with DLC coating protects the UHMWPE surface. However, the DLC coating causes severe Co–Cr–Mo wear. Coating both the sliding surfaces with DLC coating reduces the wear rates of the sliding surfaces to a greater extent. The DLC-coated UHMWPE with prior carbon implantation did not show any superior behaviour over that without prior carbon implantation.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Diamond-like carbon; Orthopaedic implants; Tribology; UHMWPE

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) sliding against metal/ceramic counter-face is very common in total joint replacements. The metal femoral head sliding against UHMWPE acetabular cup displays low coefficient of friction, but exhibits relatively high polymer wear rate [1–3]. These polymer wear debris leads to osteolysis (loss of bone material in the vicinity), which results in aseptic loosening and thus failure of the implant. Therefore, research works are being carried out to reduce the wear rate and thus improve the life of artificial joints by effective surface treatments of the sliding pairs [4–10]. Some of the major focuses are hard (for example diamond-like carbon, DLC) coating on one or either of the sliding surfaces [4–8] and surface hardening of the sliding components by ion implantation [9,10]. Our earlier research work revealed that by depositing relatively hard, smooth, low stress DLC coating on Co–Cr–Mo surface alone does not improve the wear resistance of the Co–Cr–Mo/UHMWPE sliding pair [11]. Hauert [12] has summarized the biological applications of DLC coating in a review report.

In this study, we attempt to improve the wear resistance of the sliding surfaces by surface modification of either UHMWPE or both the sliding surfaces, mainly by DLC coating and are discussed in this paper. The key motivation behind the investigation of DLC on UHMWPE is that the biocompatibility of PE is well understood compared to that of Co–Cr–Mo, in addition to the low material and manufacturing cost of PE implants over that of Co–Cr–Mo implants. In the case of DLC-coated stainless steel implants, one can imagine the intensity of wear that occurs after any accidental failure of DLC coating.
In this work, a comparative study on the tribological behaviour of two different types (with and without prior C-ion implantation) of DLC-coated UHMWPE has been tested. The results were also compared with that of untreated UHMWPE sliding against uncoated Co–Cr–Mo alloy disk. This is mainly to see whether the surface modification of UHMWPE enhances the frictional and wear behaviour over that of the uncoated polyethylene. However, the study did not show significant improvement in the friction and wear. Therefore, tribological evaluations were carried out with the abovementioned surface modified polymers against DLC-coated Co–Cr–Mo alloy and the results are compared with that of the unmodified Co–Cr–Mo/UHMWPE sliding pair.

2. Experimental details

2.1. Materials

The Co–Cr–Mo alloy (BioDur CCM Plus) rod of 30 mm diameter was supplied by the Carpenter Technology. The metal rod was cut into 30 mm diameter discs with 3 mm thickness. The disks were ground and polished to obtain mirrorlike smoothness. The grinding and polishing were done in many stages. First step of grinding was done with 240 grit silicon carbide abrasive paper, followed by 800 and 1200 grit abrasive papers. Subsequently, the grounded surfaces were polished with coarse and fine alumina solution to get mirrorlike smoothness. The polished substrates were cleaned with soap solution, followed by water, acetone, isopropyl alcohol and DI water in an ultrasonic bath tank and dried with nitrogen blow off gun. The samples were then analyzed for its roughness using an ultrasonic bath tank and dried with nitrogen blow off gun. The average surface roughness of the samples were maintained at around 0.01–0.02 μm.

Medical grade UHMWPE rod of 6.35 mm diameter was cut into 14.5-mm-long pieces and one end of the pins were machined into hemispherical shape for conformal sliding contact. The machining was done using computer-numerical control (CNC) machine. In order to maintain the surface roughness of all the samples constant, the pinheads were not further polished. The average surface roughness of the pinhead is relatively high and is approximately 3 μm. The reasons for choosing PE pin instead of Co–Cr–Mo pin is due to the uncertainty of mechanical press on the polymer (as the PE is soft) due to loading and that may result in an increased wear track depth; in addition to the difficulty of machining the hard Co–Cr–Mo pins with hemispherical ends.

The experiments were carried out in simulated body fluid (SBF) (also known as the Kokubo solution), which was prepared by dissolving reagent grade chemicals of sodium chloride (NaCl), sodium hydroxide carbonate (NaHCO₃), potassium chloride (KCl), dipotassium hydrogen phosphate (K₂HPO₄·3H₂O), magnesium chloride hexahydrate (MgCl₂·6H₂O), calcium chloride dihydrate (CaCl₂·2H₂O), and sodium sulphate (Na₂SO₄), into distilled water to obtain the inorganic ion concentrations close to that in blood plasma. The pH of SBF was adjusted to 7.00 by adding tris-(hydroxymethyl) aminomethane, and by subsequent addition of 5 N HCl solution [13]. Many research reports indicate that the type of lubricant has significant effect on the tribological behaviour [14,15]. Scholes et al. [14] showed the differences in the lubrication mechanisms and friction with two different lubricants (carboxy methyl cellulose and bovine serum), and suggest that the variation is due to the protein adsorption. Ahlroos and Saikko [15] used a three-axis hip simulator and evaluated the tribological behaviour of soybean lecithin and soy protein as lubricants, and the results were compared with that of bovine serum. In our experiments, we used SBF, which does not contain any proteins. This is a comparative study we carried out mainly to evaluate the effect of DLC coating on either or both the sliding surfaces.

2.2. Preparation of DLC film

In this study, we have prepared relatively hard, low stress, thick DLC coatings using filtered cathodic vacuum arc (FCVA) technique in conjunction with high substrate pulse biasing. The pulse biasing was done with the help of a commercially available plasma immersion ion implantation (PI³) system supplied by ANSTO, Australia. The duty cycle and pulse width of the driving square pulse. More information on the specific plasma immersion ion implantation is reported elsewhere [16,17].

The films were deposited using the FCVA system, which is described in detail elsewhere [18]. The carbon plasma for the DLC films was obtained from a graphite target of 99.999% purity. The substrates were precleaned with acetone, followed by alcohol and deionised water, and blown dry using nitrogen gas. The cleaned substrates were placed in the deposition chamber. The chamber was then evacuated to a system base pressure below 3 × 10⁻⁴ Pa, but increased to 2 × 10⁻³ Pa during deposition. The approximate deposition rate of DLC coating is about 27 nm/min. More details of the qualities of the coatings with deposition conditions are reported in our earlier work [19–21].

Some of the polished Co–Cr–Mo alloy disks were coated with 2-μm-thick DLC using FCVA system in conjunction with a negative substrate pulse bias of −3 kV, 600 Hz and 25 μs (pulse width), and some were left aside uncoated but mirrorlike polished. About six polymer pins were implanted with carbon for 10 min with a substrate bias of −10 kV, 900 Hz and 25 μs (duty cycle: 2.25%). The implantation was carried out by placing the samples parallel (0°) to the plasma direction (see Fig. 1). This is done mainly to achieve implantation and to avoid deposition. The approximate dose read from the system computer is 1.2 × 10¹⁷ ions/cm². After implantation, the samples were placed perpendicular (90°) to the plasma direction to deposit...
DLC coating. Six-micrometer-thick DLC films were prepared on them in conjunction with substrate pulse biasing of −3 kV, 600 Hz and 25 µs (duty cycle: 1.5%). Another set of six UHMWPE (unimplanted) pins were deposited with DLC coating of 6 µm thick in conjunction with substrate pulse bias of −3 kV, 600 Hz and 25 µs. Some of the UHMWPE pins were left aside untreated.

2.3. Tribological characterization

A commercially available unidirectional pin-on-disk tribometer (supplied by CSM Instruments Ref. [22]), has been used to study the frictional and wear characteristics of different combinations of sliding pairs, to examine whether any of the surface modified sliding pair display improved friction and wear compared to that of the existing orthopaedic sliding pair of Co–Cr–Mo/UHMWPE. All the tests were carried out with a constant load of 5 N with a linear speed of 3 cm/s on a 5 mm (radius) wear track in simulated body fluid. Prior to testing, all the UHMWPE pins were soaked in SBF for more than 2 weeks. The dynamic coefficient of friction values were recorded as a function of sliding distance. The wear rates of the UHMWPE pins and disks were calculated, respectively, from the change in pin-end geometry and the wear track cross-sectional area.

3. Results and discussion

3.1. Tribological characteristics

The tests were grouped into two categories: (1) unmodified as well as DLC-coated UHMWPE pins with and without prior C-ion implantation sliding against uncoated Co–Cr–Mo alloy, (2) DLC-coated UHMWPE pins with and without prior C-ion implantation sliding against DLC-coated Co–Cr–Mo alloy.

3.1.1. Unmodified and DLC-coated UHMWPE with and without prior C-ion implantation sliding against uncoated Co–Cr–Mo alloy

Fig. 2 shows the short span dynamic friction spectra of unmodified and DLC-coated UHMWPE with and without prior C-ion implantation sliding against the uncoated Co–Cr–Mo in simulated body fluid. It can be seen that the unmodified UHMWPE displays the lowest friction coefficient of approximately 0.05. The two DLC-coated UHMWPE pins display friction coefficients in the range of 0.12 to 0.16, which is approximately two to three times that of the unmodified UHMWPE. Table 1a shows the summary of the friction coefficient and wear rate based on long-term tribological evaluation of 1.2 km of sliding.

It can also be seen that the wear resistance of the polymer counter-surface was increased to a greater extent by the DLC coating. Almost no wear scar was observed on the DLC-coated UHMWPE counter-faces, except for the transfer layer in one of the cases. However, the wear rate of Co–Cr–Mo was increased in the case of DLC-coated UHMWPE with prior carbon ion implantation. We have observed significant difference in the tribological behaviour of the two DLC-coated polymer pins (with and without prior ion implantation) and are discussed in detail below.

The average coefficients of friction of DLC-coated UHMWPE with and without prior carbon implantation are approximately 0.156 and 0.122, respectively. The friction of the DLC-coated UHMWPE with prior carbon implantation displayed large fluctuations in the dynamic coefficient of friction in the initial running-in. This difference might probably be due to the morphology of the pin end. The implantation might have caused initial surface
roughening and that might have resulted in rougher DLC coating compared to the unimplanted sample. The morphology of the two pinheads before the wear testing is shown in Fig. 3.

The DLC-coated UHMWPE sample with prior carbon implantation showed a material transfer layer on the pinhead, which was not observed in the case of that without prior C-ion implantation. In order to explain the material transfer layer, the wear tracks of the respective sliding counter-faces, i.e., Co–Cr–Mo disks were examined (see Fig. 4). In the case of wear track created on the Co–Cr–Mo by the DLC-coated UHMWPE counter-face with prior ion implantation (Fig. 4a) shows severe wear of Co–Cr–Mo and from the wear scar one can suggest that the abrasive wear mechanism dominates. However, the wear track created by the DLC-coated UHMWPE without prior ion implantation shows slight surface roughening without much wear (see Fig. 4b), and which reveals adhesive wear mechanism. The reason for the difference in the wear mechanism is quite unclear except for the differences in surface roughness.

Comparing the total wear particles generated from both the sliding surfaces (see Table 1a), we can see that the DLC-coated UHMWPE with prior carbon ion implantation generates only half of that generated by the unmodified UHMWPE. While the DLC-coated UHMWPE without prior carbon ion implantation produce even lesser debris. However, in such cases, toxicity of the particle (UHMWPE or Co–Cr–Mo) outweighs the amount of wear debris if one of the materials is comparatively more toxic than the other.

The above experimental results reveal that by modifying the polymer surface by DLC coating with or without prior C-ion implantation do not reduce the friction but reduce the total wear of the material pair to a certain extent. The DLC coating with prior carbon ion implantation is worse than that without. However, the experiments showed that the DLC coating prepared on polymer pins using FCVA in conjunction with high substrate pulse bias are intact even after long-run tribological tests. This led us to study the tribology of DLC-coated polymer pin with and without prior carbon implantation against DLC-coated Co–Cr–Mo alloy; aiming to further improve the tribological performance.

<table>
<thead>
<tr>
<th>Sliding pairs</th>
<th>Counter-face (disk)</th>
<th>Average coefficient of friction</th>
<th>Wear rate of the disk (mm$^3$/Nm)</th>
<th>Wear rate of the pin (mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static sliding partner (hemispherical ended pin)</td>
<td>Uncoated Co–Cr–Mo</td>
<td>0.053</td>
<td>No wear marks</td>
<td>1.23 × 10$^{-6}$</td>
</tr>
<tr>
<td>DLC-coated (6 μm) Unmodified UHMWPE pin</td>
<td>Uncoated Co–Cr–Mo</td>
<td>0.156</td>
<td>6.07 × 10$^{-7}$</td>
<td>No wear marks</td>
</tr>
<tr>
<td>DLC-coated (6 μm) UHMWPE pin with prior C-ion implantation</td>
<td>Uncoated Co–Cr–Mo</td>
<td>0.122</td>
<td>–</td>
<td>No wear marks</td>
</tr>
</tbody>
</table>

(b) Friction and wear characteristics of the DLC-coated UHMWPE pins with and without prior C-ion implantation sliding against DLC-coated Co–Cr–Mo in simulated body fluid (load: 5 N, speed: 3 cm/s on 5 mm wear track, sliding distance: 1.2 km)

<table>
<thead>
<tr>
<th>Sliding pairs</th>
<th>Counter-face (disk)</th>
<th>Average coefficient of friction</th>
<th>Wear rate of the disk (mm$^3$/Nm)</th>
<th>Wear rate of the pin (mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC-coated (6 μm) UHMWPE pin with prior C-ion implantation</td>
<td>DLC-coated Co–Cr–Mo</td>
<td>0.052</td>
<td>No wear marks</td>
<td>2.4 × 10$^{-10}$</td>
</tr>
<tr>
<td>DLC-coated (6 μm) UHMWPE pin without prior C-ion implantation</td>
<td>DLC-coated Co–Cr–Mo</td>
<td>0.056</td>
<td>No wear marks</td>
<td>No wear marks</td>
</tr>
</tbody>
</table>

Fig. 3. DLC-coated UHMWPE with (left) and without (right) C-ion implantation.

Fig. 4a. Wear track created on the Co–Cr–Mo disk by the DLC-coated UHMWPE counter-face with prior ion implantation.

Fig. 4b. Wear track created by the DLC-coated UHMWPE without prior ion implantation.
3.1.2. DLC-coated UHMWPE with and without prior C-ion implantation sliding against DLC-coated Co–Cr–Mo alloy

The dynamic friction spectra of the DLC-coated UHMWPE with and without prior carbon implantation is given in Fig. 5. It is quite obvious from the figure that the average coefficient of friction of the sliding pairs is very low of approximately 0.05. No obvious difference in the friction was observed between the two DLC-coated UHMWPE pins. Our earlier studies showed that the friction and wear of unmodified UHMWPE sliding against DLC-coated Co–Cr–Mo is worse than that of uncoated Co–Cr–Mo sliding against unmodified UHMWPE [11]. So the above results are compared with that of uncoated Co–Cr–Mo sliding against unmodified UHMWPE. In terms of friction coefficient, the values are quite comparable. All the three sliding pairs show an average friction coefficient in the range of 0.053–0.056, where the deviation is within the error limit.

However, by comparing the wear rates (see Table 1b), the DLC-coated UHMWPE pins and their respective DLC-coated Co–Cr–Mo counter-face displayed negligible wear rates, while the unmodified UHMWPE pin showed very high wear rate. The study suggests that the sliding surfaces can be protected from wear to a greater extent by DLC coating.

3.2. Morphology of pinheads after the wear tests

As there was no obvious wear scar on the DLC-coated UHMWPE after the friction test, we have considered negligible wear rate. However, in the case of unmodified UHMWPE, the wear scar was very obvious. In order to have a comparison and detailed study, the pinheads after the wear tests were analyzed optically and are shown in Fig. 6. The images were taken with a magnification of 20, except for one pin.

Fig. 6a shows the wear scar of the unmodified UHMWPE pin, and it is quite obvious from the figure that
abrasive wear mechanism dominates. As the wear scar diameter was larger, optical images were also captured with a lower magnification of 5 so as to see the whole wear scar. Fig. 6b and c displays the wear scars of DLC-coated UHMWPE with and without prior carbon implantation sliding against uncoated Co–Cr–Mo. The DLC-coated UHMWPE with prior C-implantation shows a transfer layer on the pin, while the DLC-coated UHMWPE without prior C-ion implantation did not form any such layer. The surface roughening due to implantation could be the probable reason for the difference in the surface morphology. The transfer layer could be formed from the Co–Cr–Mo counter-face. However, as the layer is black in colour, we believe that there would be a large amount of carbon wear debris attached to it. Fig. 6d and e shows the DLC-coated UHMWPE with and without prior carbon implantation sliding against DLC-coated Co–Cr–Mo. Both the DLC-coated polymer pins did not show any significant wear scar. However, the DLC-coated polymer pins looks slightly polished due to the rubbing against similar hardness material, i.e., DLC.

4. Conclusion

The study suggests that by coating only one of the sliding surfaces with DLC will not improve the tribological characteristics of the UHMWPE/Co–Cr–Mo sliding pair significantly. The wear resistance of UHMWPE is found to be increased to a greater extent by the DLC coating on it but the generation of wear particles from the counter-face, i.e., Co–Cr–Mo is a major drawback. However, by coating both
the sliding surfaces with low stress (~ 0.5 GPa), relatively hard (~ 28 GPa) and smooth DLC coating improves the frictional behaviour as well as the wear resistance of the sliding pair significantly. The study suggests that by coating (adhesive, thick) both the polymer as well as the metal surfaces of the sliding pair with DLC could be a choice to prolong the life of the Co–Cr–Mo/UHMWPE implants. This requires doing much more experiments in a hip joint simulator with actual load and suitable lubricant medium.

References