Diamond-like carbon coatings with zirconium-containing interlayers for orthopedic implants

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\title{ABSTRACT}

Six types of diamond-like carbon (DLC) coatings with zirconium (Zr)-containing interlayers on titanium alloy (Ti-6Al-4V) were investigated for improving the biotribological performance of orthopedic implants. The coatings consist of three layers: above the substrate a layer stack of 32 alternating Zr and ZrN sublayers (Zr:ZrN), followed by a layer comprised of Zr and DLC (Zr:DLC), and finally a N-doped DLC layer. The Zr:ZrN layer is designed for increasing load carrying capacity and corrosion resistance; the Zr:DLC layer is for gradual transition of stress, thus enhancing layer adhesion; and the N-doped DLC layer is for decreasing friction, squeaking noises and wear. Biotribological experiments were performed in simulated body fluid employing a ball-on-disc contact with a Si\textsubscript{3}N\textsubscript{4} ball and a rotational oscillating motion to mimic hip motion in terms of gait angle, dynamic contact pressures, speed and body temperature. The results showed that the Zr:DLC layer has a substantial influence on eliminating delamination of the DLC from the substrates. The DLC/Si\textsubscript{3}N\textsubscript{4} pairs significantly reduced friction coefficient, squeaking noise and wear of both the Si\textsubscript{3}N\textsubscript{4} balls and the discs compared to those of the Ti-6Al-4V/Si\textsubscript{3}N\textsubscript{4} pair after testing for a duration that is equivalent to one year of hip motion in vivo.

1. Introduction

Despite a high number of studies on orthopedic implants, including new materials and designs, the revision rate of orthopedic implants is still high (Smith et al., 2012; Kurtz et al., 2012). During the last five years, the number of hip and knee replacements increased by a significant percentage (20–30\%) worldwide (Kurtz et al., 2007; Canadian Joint Replacement Registry, 2015). The demand for this intervention in younger patients (ages 45–64) is increasing; they require at least 30 years of functionality, but the average lifespan of an orthopedic implant is 15–20 years, requiring multiple revision surgeries (Kurtz et al., 2007; Kremers et al., 2015). The predominant failure mode is aseptic loosening (> 50\%), a mechanism caused by inflammatory responses (osteolysis) to wear debris and metallic ions (Abu-Amer et al., 2007; Ingham and Fisher, 2000). A significant portion of the debris is generated due to cyclic and edge loading of the ball and socket joint, and the non-continuity of the prosthesis, such as the taper joint between the stem and the head (Bozik et al., 2010; Nine et al., 2014; Mischler and Munoz, 2013). Along with mechanical wear, corrosion causes accelerated chemical degradation of the interface materials (Hauert et al., 2013). Orthopedic joints face simultaneous cyclic loads and corrosive body fluid (tribo-corrosion) (Wood, 2007), and mismatched modulus of elasticity with neighboring bone structures causing stress shielding (Blau et al., 2015; Sumner, 2015; Torres et al., 2014).

Metal-on-metal orthopedics bearings (CrCoMo) are superior to metal-on-polyethylene bearings in terms of wear rate and durability (Dowson and Jin, 2006; Goldsmith et al., 2000). However, the generated metallic ions such as Cr\textsuperscript{3+} were identified as the most likely cause for DNA damage within the first couple hours after release (Lewis et al., 2007). Ti-6Al-4V is also highly biocompatible and has good mechanical properties (Zhang et al., 2015), but not suitable for tribological applications (Choudhury et al., 2016b). In the current commercial prosthesis, Ti-6Al-4V is used as a stem, and is assembled through a taper joint with a chromium-cobalt (Cr-Co) head (Fig. 1a). However, the taper joint is a key source of corrosion and wear debris.

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DLC is a promising bearing material that has excellent mechanical, tribological and biocompatibility properties (Love et al., 2013). However, low toughness and a tendency of delamination under cyclic loadings are major drawbacks of DLC for orthopedic applications (Donnet and Erdemir, 2007). Therefore, clinical reporting reveals a loadings are major drawbacks of DLC for orthopedic applications and slow oxidization were found as major reasons for these revisions (Grill, 2003; Ching et al., 2014). To overcome the limitations of a mono-layered DLC coating, interlayers and doping materials are incorporated into the DLC coating (Love et al., 2013; Donnet and Erdemir, 2007). For example, interlayers such as Titanium (Ti) (Barriga et al., 2006), Chromium (Cr) (Choudhury et al., 2015a), and Silicon Nitride (Si$_3$N$_4$) (Almeida et al., 2011) are known to reduce residual stress, thus improving adhesion. Zirconium (Zr) (Vitu et al., 2014; Sue and Chang, 1995) interlayers have an additional benefit of enhancing corrosion resistance by offering a chemically inert physical barrier between the substrate and body fluid (Choudhury et al., 2015a). Additionally, materials such as nitrogen (N) and silver (Ag) can be doped into DLC for further reducing residual stresses without compromising wear and corrosion resistance (Love et al., 2013; Donnet and Erdemir, 2007).

Our previous work (Lackner et al., 2014) showed that 32 alternating Cr and Cr$_2$N stacked layers with a thickness ratio of 2:1 have a higher resistance to cohesive and adhesive crack propagation compared to a single-layer coating. Similar multi-layered DLCs are found to be highly suitable for orthopedics implants (Choudhury et al., 2016a, 2016b). However, the presence of Cr in the coating could be potentially toxic to a human body (Nine et al., 2014). Therefore, in the current study, we have replaced Cr$_2$N$_4$ with Zr$_2$N$_2$, and have used Zr:a-C:H and N-doped DLC (a-C:N) as the second and third layer, respectively.

We hypothesize that a multi-layered N-doped DLC coating with Zr-containing interlayers will have improved adhesion strength and corrosion resistance than mono-layered DLC and bulk Ti-6Al-4V alloys. Therefore, it will have longer durability when coupled with Si$_3$N$_4$ in a replicated physiological condition of implanted joints. To verify our hypothesis, six types of multi-layered N-doped DLC coatings were fabricated on Ti-6Al-4V discs and their biotribological properties were evaluated in the presence of simulated body fluid.

2. Material and methods

The methods for this study are divided into three phases: (a) coating fabrication, (b) material and surface property characterization, and (c) biotribological investigation and post-experimental surface analysis.

2.1. Coating fabrication

Substrates of grade 5 titanium alloy (Ti-6Al-4V metal sheet, Nova Scientific, Singapore) were machined into 15 mm (length)×15 mm (width)×6 mm (height) blocks using electrical discharge machining (A30R, Sodic, Singapore). Each block went through a series of polishing processes using various grits of silicon carbide paper: grits 1000, 1200, 1500, and 2000, and finally a polishing cloth using a diamond polycrystalline suspension (0.02 µm). Before deposition, the substrates (Ti-6Al-4V) were cleaned ultrasonically in ethanol and air dried. Low-pressure (2×10$^{-3}$ Pa) plasma etching by an anode layer ion source (ALS, Veeco, Fort Collins, CO, USA) (Vitu et al., 2014) was applied first to remove organic contaminants and natural oxides on the surface in an oxygen atmosphere and then to chemically activate the surface in an argon atmosphere. Unbalanced magnetron sputtering from 4 rectangular cathodes in an industrial-scale vacuum chamber (Leybold Vacuum, Cologne, Germany) was used to deposit Zr, ZrN, Zr:DLC and N-doped DLC coatings from high purity Zr (99.99%, RHP Technology GmbH, Seibersdorf, Austria) and electrographite carbon targets (99.9%, Schunk Group, Bad Goisern, Austria), respectively.

The coatings consist of three layers: a layer stack of 32 alternating Zr and ZrN sublayers (Zr:ZrN), a layer composed of Zr and DLC (Zr:DLC), and an N-doped DLC layer. The Zr:ZrN layer is designed for increasing load carrying capacity and corrosion resistance, the Zr:DLC layer is for gradual transition of stress between Zr:ZrN and N-doped DLC layers to enhance layer adhesion, and the N-doped DLC layer is for decreasing friction, squeaking noise, and wear. A schematic diagram of the coating structure is shown in Fig. 2a. The three major layers are designed in such a way that the generated stresses can gradually distribute across the layers to help the coating survive longer.

Table 1 describes the multi-layer coatings and associated thickness of each layer. Fig. 2b shows a scanning electron microscopy (SEM) image of the cross-section of sample B+ taken from 52° oblique angle, showing the layered structure of the DLC. In the 1st layer, the Zr:ZrN has three thickness ratios: 1:1 (samples B+ and C+), 1:2 (samples E+ and F+), and 1:4 (samples H+ and I+). In the 2nd layer, samples B+, E+, and H+ have lower DLC content and samples C+, F+, and I+ have higher DLC content. The N-doped DLC layer is the same for all coatings.

2.2. Material and surface property characterization

The average roughness (Ra) and root mean square roughness (Rq) were measured using a laser scanning confocal microscope (LSCM, VK-X260, Keyence, USA). The wear tracks were mapped using both the LSCM and an atomic force microscopy (AFM, Bruker Dimension Icon, USA). The hardness and modulus of elasticity was measured using an instrumented nanoindenter (TriboIndenter, Hysitron Inc. Minneapolis, MN) with a diamond Berkovich tip with about 100 nm tip radius. Normal loads of 1000–5000 µN were chosen (Vitu et al., 2014; Beake et al., 2015) for observing the nanoindentation behaviors with 5 indentation tests under the same test condition.

Water contact angle measurements were performed using the
sessile drop method (OCA 15 plus, DataPhysics Instruments GmbH, Filderstadt, Germany). Water droplets of 1 µL volume were created through a syringe, and the deposited droplet was imaged with a digital camera. The software automatically calculates left and right water contact angles. An average contact angle was calculated from 14 separate measurements on each sample.

The Raman spectra were measured with 785 nm Raman excitation (QE Pro-Raman Ocean Optics, USA). A laser power of 0.5 W with a spot size of ~165 µm in diameter and a scanning time of 35 sec were used for all measurements. Five spots on each sample were measured with the same setup. The intensities of the G and D peaks (IG≈1560 cm\(^{-1}\) Raman shift and ID≈1360 cm\(^{-1}\) Raman shift) were first identified, and the ratios of IG/ID or sp\(^3\)/sp\(^2\) hybridization were then calculated for each measurement point. It is noted that the ratio of IG/ID indicates a deposited or a graphitized and delaminated DLC. A low ratio indicates DLC is deposited, and it increases as graphitization and delamination progress (Lackner et al., 2014; Choudhury et al., 2016a; Beake et al., 2015). An X-ray photoelectron spectroscopy (XPS) (D-65232, Omicron GmbH, Traunusstein, Germany) mapping was performed to evaluate DLC content of the Zr:DLC layer.

Table 1: Composition and thickness of DLC sublayers.

<table>
<thead>
<tr>
<th>Sample types</th>
<th>1(^{st}) layer; thickness (Zr:ZrN sublayers)</th>
<th>2(^{nd}) layer; thickness (Zr:DLC composition)</th>
<th>3(^{rd}) layer; thickness (N-doped DLC)</th>
<th>Total thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+</td>
<td>1:1; 2321 nm</td>
<td>Low-DLC; 789 nm</td>
<td>a-C:N; 362 nm</td>
<td>3472 nm</td>
</tr>
<tr>
<td>C+</td>
<td>1:1; 2321 nm</td>
<td>High-DLC; 771 nm</td>
<td>a-C:N; 362 nm</td>
<td>3454 nm</td>
</tr>
<tr>
<td>E+</td>
<td>1:2; 2377 nm</td>
<td>Low-DLC; 789 nm</td>
<td>a-C:N; 362 nm</td>
<td>3528 nm</td>
</tr>
<tr>
<td>F+</td>
<td>1:2; 2377 nm</td>
<td>High-DLC; 771 nm</td>
<td>a-C:N; 362 nm</td>
<td>3510 nm</td>
</tr>
<tr>
<td>H+</td>
<td>1:4; 2306 nm</td>
<td>Low-DLC; 789 nm</td>
<td>a-C:N; 362 nm</td>
<td>3457 nm</td>
</tr>
<tr>
<td>I+</td>
<td>1:4; 2306 nm</td>
<td>High-DLC; 771 nm</td>
<td>a-C:N; 362 nm</td>
<td>3439 nm</td>
</tr>
</tbody>
</table>

The tribological experiments were performed using a Universal Mechanical Tester (UMT-2, Bruker Nano Surfaces, San Jose, CA, USA). This equipment is capable of recording applied loads, frictional forces, temperatures, acoustic emission signals and contact resistances. The friction force and applied normal load during sliding were recorded every 10 milliseconds. The COFs were calculated from the ratio of friction force vs. normal load at each applied normal load. Fig. 3 shows the UMT-2 with a sample under load and two wear tracks. Before the tribology test, the specimen was cleaned ultrasonically according to the following procedure: 15 min in detergent (95% deionized water), 10 min in ethanol, 10 min in isopropyl alcohol (IPA), 5 min with deionized water, and dried using nitrogen gas. Wear tests were carried out with a simulated body fluid, which was prepared by adding γ-globulin powder (1.4 g/100 ml) into 30% fetal bovine serum and 70% deionized water, by volume. The solution was placed on a magnetic stir plate (VWR, Radnor, PA, USA) at 400–600 revolutions per min (rev/min) for 5 min in order to disperse the protein into the bovine serum homogenously.

Fig. 3. Biotribological experimental setup: (a) Universal Mechanical Tester (UMT-2) and (b) a Ti-6Al-4V sample under load with a 40° oscillation motion mimicking a walking gait cycle. The dimensions of bulk Ti-6Al-4V sample is 32 mm in diameter and 6 mm in height.
To mimic a gait of human walking, tribological tests were conducted using an oscillation angle between 32.4 and 39.6°, a speed of about 23 mm/s at a temperature of 37° C in the simulated body fluid. The details of the experiment were described in Table 2. An applied Hertzian contact pressure of 0.62–1.20 GPa against Si3N4 balls with 6.35 mm diameter were used in this experiment, which are much higher than that of a 28 mm diameter hip prosthesis in similar material combinations (0.17–0.19 GPa).). Each experiment was performed for 8 h, which is equivalent to 1–2 months’ gait cycles of osteoarthritis patients considering an average of 0.9 million cycles per year (Schmalzried et al., 1998). Therefore, by applying 4–6 times higher contact pressures, the total number of cycles of the present experiment is assumed to be equivalent to one year use of one joint supporting the total body weight.

3. Results

3.1. Mechanical and surface properties

The nano-mechanical properties of the DLC coated Ti-6Al-4V and uncoated Ti-6Al-4V are shown in Table 3. It can be seen that the average hardness of the DLCs are 10.3–13.2 GPa, which is 2–3 times higher than that of the bulk Ti-6Al-4V (4.8 GPa). The modulus of elasticity also increased with DLC coating, but did not increase proportionally with hardness. Consequently, the plasticity index (hardness/elasticity) of the DLC-coated samples increased significantly from the uncoated substrates. Among them, the highest average plasticity index at nanoindentation loads of 1000–5000 µN were found to be 0.104 for C+ and I+, followed by 0.102 for F+. On the other hand, the bulk Ti-6Al-4V has the lowest plasticity index of 0.044, followed by that of E+ (0.088), B+ (0.089) and H+ (0.098).

The nanoindentation load-displacement curves of F+ (Fig. 4a) at 1000–5000 µN indentation loads show no significant creep (Ma et al., 2009). In summary, the high-DLC group displays relatively lower hardness values but higher plasticity index. According to the Archard wear equation (Stachowiak and Batchelor, 2013), hardness is the most influential determining factor that is inversely proportional to the wear rate. However, according to modern literature, a plasticity index plays a critical role in wear rate, especially for a hard coated surface such as DLC (Ching et al., 2014). The surface roughnesses of all samples are similar. Fig. 4b shows a typical surface topography of F+ measured using AFM. The Ra is 15 nm with a standard deviation (SD) of 5 nm. The Rq is 17 nm with a SD of 6 nm. The water contact angles are also very similar for all DLCs with an overall average of 77.6° and SD of 3°, which is expected since the top layers are the same DLC material. The water contact angles of DLCs are similar to that reported in literature (Choudhury et al., 2016a).

3.2. Coating characterization

Fig. 2b is an SEM cross-sectional image of a multi-layered DLC (sample B+) taken at 52° oblique angle showing the layered structures

Table 2
Details of biotribology experiment.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>Hertzian contact pressure (GPa)</th>
<th>Hertzian contact pressure of 28 mm hip joint prosthesis (Mak and Jin, 2002; Shigley, 2011)</th>
<th>Rev/min</th>
<th>Equivalent speed (mm/s)</th>
<th>Oscillation angle (°)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.62</td>
<td>0.17 GPa for 80 kg bodyweight</td>
<td>12</td>
<td>22.6</td>
<td>39.6</td>
<td>37°C</td>
</tr>
<tr>
<td>5</td>
<td>1.07</td>
<td>0.19 GPa for 100 kg bodyweight</td>
<td>10</td>
<td>23.0</td>
<td>36.0</td>
<td>37°C</td>
</tr>
<tr>
<td>7</td>
<td>1.20</td>
<td>9</td>
<td>22.6</td>
<td>32.4</td>
<td>37°C</td>
<td></td>
</tr>
</tbody>
</table>

Table 3
Average hardness, modulus of elasticity, surface roughness and wettability for the experimental samples.

<table>
<thead>
<tr>
<th>Sample types</th>
<th>Indentation loads (µN)</th>
<th>Hardness (GPa)</th>
<th>Modulus of elasticity (GPa)</th>
<th>Plasticity index</th>
<th>Roughness (Ra) nm</th>
<th>Roughness (Rq) nm</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+</td>
<td>1000–5000</td>
<td>12.9 ± 1.67</td>
<td>162.01 ± 8.34</td>
<td>0.089</td>
<td>15 ± 5</td>
<td>17 ± 6</td>
<td>79.2 ± 4.7</td>
</tr>
<tr>
<td>C+</td>
<td>10.3 ± 1.2</td>
<td>147.70 ± 7.61</td>
<td>160.15 ± 9.44</td>
<td>0.104</td>
<td></td>
<td></td>
<td>77.3 ± 2.7</td>
</tr>
<tr>
<td>E+</td>
<td>12.6 ± 0.6</td>
<td>124.74 ± 6.17</td>
<td>134.26 ± 8.43</td>
<td>0.102</td>
<td></td>
<td></td>
<td>77.3 ± 3.2</td>
</tr>
<tr>
<td>F+</td>
<td>13.2 ± 0.62</td>
<td>146.60 ± 7.40</td>
<td>134.26 ± 8.43</td>
<td>0.098</td>
<td></td>
<td></td>
<td>77.3 ± 3.8</td>
</tr>
<tr>
<td>H+</td>
<td>11.1 ± 1.1</td>
<td>115.21 ± 4.43</td>
<td>115.21 ± 4.43</td>
<td>0.104</td>
<td></td>
<td></td>
<td>80.8 ± 4.0</td>
</tr>
<tr>
<td>I+</td>
<td>10.7 ± 1.2</td>
<td>115.21 ± 4.43</td>
<td>115.21 ± 4.43</td>
<td>0.104</td>
<td></td>
<td></td>
<td>73.2 ± 3.2</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>4.8 ± 0.2</td>
<td>79.2 ± 4.7</td>
<td>77.3 ± 2.7</td>
<td>77.3 ± 3.2</td>
<td></td>
<td></td>
<td>77.3 ± 3.8</td>
</tr>
</tbody>
</table>

Fig. 4. Nanomechanical behavior and surface topography: (a) load-displacement curves and (b) AFM image for sample F+.
and Table 1 shows the thicknesses of each layer. XPS spectra of Zr:DLC layers (2nd layer) are shown in Fig. 5, which represents the corresponding chemical states. For example, ZrO$_2$ and sub-oxide of ZrO$_2$ are found in the XPS region: Zr3d (Fig. 5c and d). These sub-oxides of ZrO$_2$ were generated by the argon ion bombardment during sputtering process.

The XPS results revealed that the low-DLC layer had 36.83% higher peak area of ZrO$_2$ compared to that of high-DLC layer. On the other hand, the high-DLC layer have higher sp$^3$/sp$^2$ ratio (1.06) compare to that of (0.82) low-DLC layer. Raman spectra and their resultant ID/IG ratio of the DLCs (3rd layer) are shown in Fig. 6. From Fig. 6(b), it is confirmed that the 2nd layer has an influence on the ID/IG ratio. The DLCs with high-DLC exhibit a higher ID/IG ratio (1.1–1.2) compared to that of low-DLCs (0.73–0.87). Importantly, all compositions of the fabricated DLC such as ZrO$_2$, ZrN and a-C:N are non-toxic for a human body (Stachowiak and Batchelor, 2013).

### 3.3. Friction and acoustic signal analysis

The comparison of average coefficient of friction (COF) under an applied normal load of 1, 5 and 7 N is shown in Fig. 7. COFs were calculated based on the measured friction forces and applied normal loads. The uncoated Ti-6Al-4V yielded a higher COF (0.30 ± 0.014) compared to the DLC coated samples under an applied normal load of 1 N. Among the DLCs, the COFs of I$^+$ is the lowest (0.23 ± 0.004), followed by that of F$^+$, C$^+$, E$^+$, and B$^+$. The high-DLC group (C$^+$, F$^+$ and I$^+$) process slightly lower COFs compared to the low-DLC group (B$^+$, E$^+$, H$^+$). At a 5 N normal load, the overall COF values of DLCs lowered significantly compared to that of bulk Ti-6Al-4V (0.24 ± 0.074). Sample F$^+$ has the lowest COF (0.109 ± 0.013), which is about 50% lower than that of the uncoated Ti-6Al-4V. Moreover, the COF of the uncoated Ti-6Al-4V have large variations, whereas the COF of F$^+$ is mostly stable. Finally, at 7 N normal load, the COFs of the low DLC group dropped further, thus yield a higher difference (about 150% lower) from that of Ti-6Al-4V. F$^+$ remained to have the lowest COFs (0.09 ± 0.0008) along with a stable profile. In summary, all DLC coated samples reduced COF at higher loads and the high-DLC group yielded lower COFs compared to low-DLC group.

The acoustic emission (AE) signal provides a powerful evidence of interfacial behavior. Fig. 8a represents a comparison of AE signals for all samples. It can be clearly seen that a strong periodic AE signal (0.2–0.3 V) is generated from the Ti-6Al-4V/Si$_3$N$_4$ pair. In comparison, the AE signals from DLC/Si$_3$N$_4$ pairs remain low (<0.05 V), which...
were mainly from the background noises. A recorded video of ‘squeaking noises’ is included in the supplemental materials. Fig. 8b shows the AE signal and associated COF of Ti-6Al-4V, from which it can be identified that the peak values of AE are formed during the backward strokes.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.jmbbm.2017.01.023.

3.4. Wear track on ball

The worn areas on the Si₃N₄ balls and the associated dimensions are shown in Fig. 9. Despite a much higher hardness of the Si₃N₄ (15.5 GPa) compared to its counterpart Ti-6Al-4V (4.8 GPa), a substantial size of worn area (elliptical shaped area of 1.466 mm²) was formed on the Si₃N₄ ball. On the other hand, the worn areas associated with corresponded DLCs are (in ascending order): 0.046 mm² (F⁺) < 0.047 mm² (C⁺) < 0.053 mm² (B⁺) < 0.054 mm² (I⁺) < 0.057 mm² (H⁺) < 0.058 mm² (E⁺). Numerically, the wear track area associated with F⁺ is only 3.15% of that of associated with Ti-6Al-4V. From this result, it can be estimated that the multi-layered DLC samples significantly reduced the wear rate of the counterpart Si₃N₄ balls compared to T-6Al-4V.

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3.5. Wear on disc and sign of wear debris

The images of wear tracks under 1, 5, and 7 N loads are shown in Fig. 10. Interestingly, all of the low-DLC surfaces were found to have delamination (Fig. 10a, c and e). On the other hand, all high-DLC surfaces are found not to have any delamination (Fig. 10b, d and f). Within the low-DLC samples, E+ exhibits severe delamination regardless of applied loads. The AFM images give further details of delaminated and un-delaminated wear tracks. Fig. 11a shows the delamination segment within the wear track and it is clearly seen that the edge is very sharp (height ~400 nm), which can be distinguished from the un-delaminated segment of the wear track. The un-delaminated segments have some abrasive scratches with a depth of around 40 nm (Fig. 11b). AFM images also confirm no delamination occurred in the wear tracks of high-DLC substrates. The wear tracks were formed due to plastic deformation of the materials under the applied contact pressure (Fig. 11c).

Fig. 12 exhibits a comparison of dimensions of wear tracks for all experimental samples. A groove-type of wear track (~30.18 µm deep and ~843 µm wide) was formed on the uncoated Ti-6Al-4V disc under 7 N normal loads. As expected, the wear tracks of DLC coated samples were significantly smaller compared to that of the uncoated sample when tested under the same applied normal loads. From Fig. 12, it is confirmed that the depth and width of the wear track increase with the applied normal loads. At all normal loads, the wear width and depth of all DLC coated samples are much smaller than those of the uncoated sample. F+ sample has the best wear performance. In comparison with Ti-6Al-4V, the width/depths of the wear track of F+ were 18.4%/6.9% at 1 N load, 21.4%/4.3% at the 5 N load, and 21.6%/3.6% at the 7 N load. Furthermore, the significant portion of the depth was formed mainly due to plastic deformation of DLC, confirmed by the AFM image. The post experimental specimen immediately after the experiment (Fig. 13) showed generated debris from the ‘Ti-6Al-4V/Si3N4’ pairs, whereas no visible debris were generated from any of the ‘DLC/Si3N4’ pairs.

4. Discussion

The strength of this study is that it includes well-defined multilayered functional DLCs. The 1st layer consisted of 32 sublayers of Zr:ZrN, which are responsible for preventing the unwanted slow progressive bio-corrosion, thus increasing the bonding strength (Kop and Swarts, 2009; Love et al., 2013). The second layer consisted of Zr and DLC composites, which were fabricated for reducing fatigue residual stress (Lackner et al., 2014). Within the second layer, the high-DLCs were 18 nm thinner than that of low-DLCs due to the higher portion of carbon flows. The top layer consisted of N doped DLC was same for all DLCs. Importantly, neither the substrate (Ti-6Al-4V) nor the coating elements (Zr, ZrN, a:C-N) have any issue of toxicity to human body (Love et al., 2013; Schmalzried et al., 1998).

We selected Si3N4 as a counterpart materials instead of CrCoMo, Al2O3 or UHWMPE (Bal et al., 2008), which are most common in orthopedics bearing interface. Si3N4 has better mechanical properties than Al2O3 and is a better tribological counterpart with DLC than CrCoMo or UHWMPE (Choudhury et al., 2016b; Morillo et al., 2009; Bal and Rahaman, 2012). We carried out ball-on-disc biotribological...
tests in a simplified form. Nevertheless, the equivalent contact pressure, speed and body temperature (37 °C) are similar to that of replaced hip joints (Love et al., 2013; Barriga et al., 2006). The oscillating motion (32–40° angles) was chosen in the experiment similar to human walking gaits in terms of gait angles (30–43°) and dynamic loadings (real magnitude and direction changes over times). Although the applied normal load was constant, the real normal loads varied due to the generated torques by the multi-directional sliding path. The simulated body fluid (bovine serum and globulin protein) having a similar composition to synovial fluid was used in the experiment (Bersoulli et al., 2015). Thus our experiment is similar to that of a modern hip simulator (Ghosh et al., 2015).

The COFs of DLC/Si₃N₄ pairs were significantly reduced (0.09–0.26) compared to those of Ti-6Al-4V/Si₃N₄ pair (0.23–0.30). These results are consistent with our previous study conducted by a pendulum hip simulator (Choudhury et al., 2015a, 2015b), where a DLC (a-C:H top layer and Cr interlayer) coated head paired with CrCoMo cup yielded COF of 0.09. Importantly, the wear rates of both Si₃N₄ balls and DLC coated disc are significantly reduced from that of the Ti-6Al-4V/Si₃N₄ pair. The worn area of Si₃N₄ ball paired with F⁺ is only 3.1% that of Si₃N₄ ball paired with Ti-6AL-4V. The experiment was performed for 8 hours per ball, thus the wear rate (area/total sliding distance) is equivalent to 70 µm²/m. This value is 4.1 and 11 times lower than that of Cr interlayered DLC/Si₃N₄ pair (286 µm²) (Choudhury et al., 2016b) and Al₂O₃/Si₃N₄ pairs (772 µm²/m) (Morillo et al., 2009), respectively. The decreased wear rate indicates that Zr multi-layered DLC coatings provide superior tribological performances to orthopedic implant applications compared to that of other published state-of-the-art surfaces. It could be because of Zr doped DLC is a dense and homogeneous low-shear carbonaceous tribolayer compared to other DLC materials.

Fig. 10. LSCM images of wear track on DLC coated samples after the biotribology tests (a) B⁺, (b) C⁺, (c) E⁺, (d) F⁺, (e) H⁺ and (f) I⁺. B⁺, E⁺ and H⁺ show sign of delamination and C⁺, F⁺ and I⁺ show no sign of delamination.
to that of pure a-C:H, and as a result, low friction and wear achieved and counterpart oxidation avoided. Vitu et al. also reported that Zr doped DLC reduced friction and wear significantly, compared with that of pure a-C:H (Vitu et al., 2014).

According to our results, Zr doped high-DLC eliminated the delamination problem. We found that low-DLCs delaminated during wear testing, leading to large variability in their ability to resist wear. On the other hand, high-DLCs had superior plasticity indexes, reduced wear rates without showing signs of delamination during wear testing. Hee et al. made a comparison study on hard coatings used in orthopedic applications, and concluded that superior plasticity index is one of the most dominating factor in yielding decreased COF and wear rate (Ching et al., 2014). In this study, wettability and surface roughness (Ra and Rq) are nearly the same for the DLCs and bulk Ti-6Al-4V. However, modulus of elasticity and plasticity index were significantly improved for the high-DLC coatings. The improved tribological performance of the high-DLC surfaces demonstrated a strong potential for the use of these coatings in orthopedic implants. Structurally, C+, F+ and I+ all have the same tribological top layer and functional layer. The only difference is the thickness ratio of Zr:ZrN (1:1 for C+, 1:2 for F+ and 1:4 for I+). ZrN is renowned for its super hardness (22.7 ± 1.7 GPa) (Chang and Wu, 2013) and cement-like behavior. It is also a good interlayer material for increasing bonding strength. However, its elastic modulus is much higher than that of Ti-6Al-4V (Morillo et al., 2009). Thus, the stress distribution at the interface between ZrN and Ti-6Al-4V was an area of potential concern. To overcome this issue, the relatively softer Zr layers were fabricated between two ZrN layers (Verma and Jayaram, 2012). From the experimental results such as material and surface properties, friction coefficient, wear of balls and discs, it is recommended that Zr:ZrN (1:2, F+) is a suitable load carrying layer structure for the multi-layered DLC.

5. Conclusion

In this study, Zr multi-layered N-doped DLCs were fabricated on Ti-6Al-4V discs using magnetron sputtering and studied in relation to their biotribological behavior in three different contact pressures mimicking replaced hip joints. It can be concluded that DLC coatings have improved hardness, plasticity index without compromising surface roughness and wettability compared to uncoated Ti-6Al-4V. As a result, the DLCs significantly reduced COF, wear rate with ball-on-disc testing, and eliminated squeaking noises under physiological loads. Materials such as highly biocompatible and corrosion resistance Zr and Zr:N are appropriate to be an interlayer of the functional DLC. The high-DLC was found to have improved delamination strength, thus more effective in further decreasing friction and wear rate. In particular, the F+/Si3N4 pair reduced 30 times of wear rate, lowered 2−2.5 times of friction coefficient and significantly eliminated squeaking compared to Ti-6Al-4V/Si3N4 pair without having any delamination after sliding equivalent to 1 year. Hence, the Zr-multilayered high-DLC can be coated on Ti-6Al-4V femoral head and Si3N4 can be used as an acetabulum cup.
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