DIAMOND-LIKE CARBON COATINGS TO ENHANCE BEARING SURFACES IN JOINT ARTHROPLASTY

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Background

- The purpose of this study was to evaluate the potential of a hard diamond-like carbon (DLC) coating to enhance a bearing surface in joint arthroplasty [1-3].
- The greater hardness of a magnesium-stabilized zirconia (Mg-PZS; ASTM F2303) substrate was hypothesized to provide a stronger coating-substrate construct than cobalt chromium alloy (CoCr; ASTM F799) also used in joint replacement.
- Mg-PZS has previously been shown to resist phase transformation and degradation, maintaining its smooth surface finish and hardness [4,5].

Experimental Details

- Ten CoCr and ten Mg-PZS never-implanted 28 mm femoral heads used in this study; half sent to commercial vendor for DLC coating, others as control heads (n = 5 per group).
- A surface oxidized zirconium alloy (OxZr; Smith & Nephew) sample TKA femoral component t was analyzed for comparison.
- Average (Sa) and root-mean-square (Sq) roughness measured by optical profilometry (3 scans per specimen).
- Reliability and repetitively measured via the average contact angle (θa) formed by a 0.25 µL droplet of distilled water [6,7].
- Resistance to abrasive wear evaluated by Vickers microhardness tests (ASTM C1327) on select samples.
- Elastic modulus (E5) and hardness (H) of the coating measured independent of the substrate by nanoindentation testing in select samples (n = 3 per group).
- Relative coating strength determined from scratch tests (ASTM C1624) as the average load causing cohesive (cracking or peeling; Lc) and adhesive (spalling or delamination; Lc) on select samples (n = 3 per group).
- Scratch width, depth, and pile-up at L = 30 mm measured by optical profilometry at 16x.
- Differences between two groups evaluated by two-sided unpaired t-test, with p < 0.05 for significance.

Results

- DLC coating on CoCr appeared to reduce surface roughness (Table 1), but trend was not significant (p < 0.10).
- Roughness of uncoated and DLC-coated Mg-PZS specimens were not significantly different.

Table 1. Roughness data at 32X and 10X (n = 5 except OxZr).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>32X Sa (nm)</th>
<th>32X Sq (nm)</th>
<th>10X Sa (nm)</th>
<th>10X Sq (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCr</td>
<td>14.0</td>
<td>22.9</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td>DLC-CoCr</td>
<td>14.0</td>
<td>29.6</td>
<td>37.9</td>
<td></td>
</tr>
<tr>
<td>Mg-PZS</td>
<td>8.12</td>
<td>17.8</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>DLC-Mg-PZS</td>
<td>8.12</td>
<td>17.8</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>OxZr TKA</td>
<td>19.4</td>
<td>38.6</td>
<td>50.6</td>
<td></td>
</tr>
</tbody>
</table>

- DLC coating significantly reduced contact angles relative to respective uncoated substrates (Figure 1; each p < 0.005).

Figure 1. Representative droplets and average contact angles for each specimen tested (n = 5 except OxZr).

- Microhardness of DLC-coated specimens increased by 18-25% (CoCr) and 27-40% (Mg-PZS; Table 2), but DLC-CoCr exhibited circumferential cracks and frequently spalled.
- Uncoated CoCr and Mg-PZS specimens were much harder at the nano-scale (H; indents 0.6-3 µm deep) than at the micro-scale (HV; indents 3-9 µm deep), likely due to surface hardening when polished by manufacturer.
- E5 and H of DLC-CoCr and DLC-Mg-PZS were significantly different and probably reflected the properties of the coating only, given coating thickness (about 3-4 µm).

Table 2. Vickers microhardness data (HV 0.5 and HV 0.3) and nanoindentation data (E5 and H, avg. ± s.D.) for each group.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>HV 0.5 (GPa)</th>
<th>HV 0.3 (GPa)</th>
<th>E5 (GPa)</th>
<th>H (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCr</td>
<td>9.28</td>
<td>7.77</td>
<td>357 ± 20</td>
<td>6.71 ± 0.13</td>
</tr>
<tr>
<td>DLC-CoCr</td>
<td>8.07</td>
<td>6.33</td>
<td>230 ± 19</td>
<td>24.5 ± 0.79</td>
</tr>
<tr>
<td>Mg-PZS</td>
<td>10.6</td>
<td>-</td>
<td>301 ± 32</td>
<td>15.3 ± 0.15</td>
</tr>
<tr>
<td>DLC-Mg-PZS</td>
<td>13.4</td>
<td>14.8</td>
<td>189 ± 7.6</td>
<td>22.9 ± 0.92</td>
</tr>
</tbody>
</table>

- In scratch tests (Table 3), both DLC-CoCr and OxZr exhibited delamination before reaching the minimum load needed for DLC-Mg-PZS to begin cracking.
- At highest loads, DLC coating on Mg-PZS exhibited peeling and recovery spallation, but did not delaminate.
- Relative coating cohesive (Lc) and adhesive fracture strength (Lc) from scratch tests (n = 3 except OxZr).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Lc – (N)</th>
<th>Lc – (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC-CoCr</td>
<td>9.74 ± 0.93</td>
<td>35.2 ± 0.65</td>
</tr>
<tr>
<td>DLC-Mg-PZS</td>
<td>41.3 ± 4.6</td>
<td>40.2 ± 2.8</td>
</tr>
<tr>
<td>OxZr TKA</td>
<td>25.5</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Figure 2. Typical scratch profiles at L = 30 N.

- Despite larger scratch width and depth relative to CoCr, DLC-CoCr significantly reduced pile-up from 2.6 to 0.43 µm, p < 0.005 (Figures 2, 3).
- Mg-PZS and DLC-Mg-PZS scratches had similar depth (0.23-0.18 µm) and width, but DLC-Mg-PZS significantly reduced pile-up from 0.53 to 0.33 µm, p < 0.005.
- The OxZr specimen exhibited 1.8 µm of pile-up and the largest scratch depth (9.8 µm).

Figure 3. Surface plots of typical scratch track at L = 30 N for A: DLC-Mg-PZS and B: OxZr. Scratch direction was from top right to bottom left. Lateral axis = 296 µm ± 200 µm; vertical axis fixed = 21 µm and amplified by 5%

Discussion

- An amorphous DLC coating on a Mg-PZS substrate has been rigorously tested and outperformed other materials used for bearing surfaces in joint replacement.
- DLC-coated Mg-PZS provided the same low roughness of its substrate while significantly improving contact angle.

Figure 4. Contact angle measurements for untreated and DLC-coated Mg-PZS.

Tables 5 and 6. Contact angle data were higher than reported elsewhere [6], but could be a result of differences in surface roughness and composition [8] or due to the reduction in residue from the cleaning process [7] used in current study.

Conclusions

- The use of Mg-PZS as a coating substrate facilitated a greater coating-substrate composite hardness and coating strength, relative to DLC-CoCr, with similar contact angles.
- Compared to the OxZr specimen, DLC-Mg-PZS specimens:
  - Exhibited lower roughness and comparable contact angle
  - Appeared to have superior resistance to abrasive wear, requiring higher loads for cohesive and adhesive fracture.
  - Displayed less potential for counterface wear, due to reduced tendency to form raised edges when scratched.