A comparative surface analysis of explanted hip joint prostheses made of different biomedical alloys

Análisis comparativo de superficies de prótesis de caderas explantadas de diferentes aleaciones biomédicas

Angela Bermúdez-Castañeda 1, Johanna Esguerra Arce 2, Adriana Esguerra-Arce 2, Sofia Valentina Vargas-Pabón 2, Juan Guillermo Ortiz-Martínez 3, David Leonardo Blanco-Estupiñán 1, Juan Guillermo Castaño 4, Stefano Mischler 5

2Departamento de Ingeniería Industrial, Escuela Colombiana de Ingeniería Julio Garavito. AK. 45 # 205-59, Autopista Norte. C. P. 14520 Bucaramanga, Colombia.
3Director, Clínica Universidad La Sabana. Autopista Norte # 7, Puente Del Común. C. P. 0815. Bogotá, Colombia
5Tribology and Interfacial Chemistry Group MER, École Polytechnique Fédérale de Lausanne. Route Cantonale. P. C. 1015. Lausanne, Switzerland

CITE THIS ARTICLE AS:


ARTICLE INFO:

Received: November 27, 2020
Accepted: March 23, 2021
Available online: March 23, 2021

KEYWORDS:

Retrieval explants; tribocorrosion; modular hip joint implants; wear; corrosion

Explantes; tribocorrosion; implantes modulares de cadera; desgaste; corrosión

ABSTRACT: The introduction of modular design in total hip arthroplasty has enabled the use of different materials in one single configuration and the adjustment of the prosthesis to the patient’s body, and facilitated medical revisions. However, modularity leads to the presence of new interfaces created between pieces in contact, raising the issue of degradation. Tribocorrosion phenomena have been identified as the main degradation mechanism due to the mechanical, chemical, and electrochemical conditions acting on the materials. In addition, conditions inside the human body are unclear, regarding electrochemical settings and the interaction between the electrochemical and mechanical action. This work is focused on the degradation of monopolar hip joint implants made from biomedical alloys such as stainless steel, Ti, and CoCr alloys. Three cases are presented and analyzed in terms of the degradation level along the trunnion length. Surface analysis done on a titanium trunnion showed a significant ploughing on the distal part, compared to what was found for stainless steel and cobalt-chromium alloys, which can produce a stuck in this area. Meanwhile, in the proximal part, wear debris is found, which suggests more movement in the internal part. Although few debris particles were identified in CoCr trunnion, a large amount of material inside the contact was observed. This could be related to the ploughing generated in the distal thread pattern, which allowed the material to come inside and outside the contact.
RESUMEN: El uso de implantes modulares de cadera ha permitido el uso de diferentes materiales en un solo dispositivo, un mejor ajuste a la anatomía del paciente y, ha facilitado los procedimientos de revisión. Sin embargo, dicha modularidad crea nuevas interfaces que pueden sufrir degradación por mecanismos triboquímicos como fretting – corrosión, por las condiciones mecánicas, químicas y electroquímicas propias del cuerpo. Actualmente, dichas condiciones no son completamente claras, ni la interacción ellas. Este trabajo se centra en el análisis de la degradación de implantes mono-polares de cadera elaborados en aleaciones biomédicas: acero inoxidable (SS), aleaciones de Ti y CoCr, en los que se analiza el nivel de degradación a lo largo de la longitud del cono femoral. El cono femoral de titanio mostró una deformación más significativa de la zona distal que causa un bloqueo entre las partes modulares, comparado con la misma zona de partes fabricadas en SS y aleaciones cobalto-cromo. Por otra parte, partículas de desgaste fueron encontradas en la parte proximal, lo que sugiere que esta es una zona bajo mayor movimiento. En el cono femoral de CoCr pudo observarse una gran cantidad de material orgánico dentro del contacto. Lo anterior pudo ser causado por un ajuste deficiente inferido por la baja deformación en los filetes de la zona distal, lo que probablemente promovió que más material entrara y saliera del contacto.

1. Introduction

Total hip arthroplasty (THA), currently a very common orthopedic intervention, dates back over 100 years. The form of hip prosthesis mainly used now was designed in the early 1960’s, and consists of a femoral stem and a polyethylene acetabular component [1, 2]. Currently, a typical hip prosthesis configuration has four parts: the stem, the femoral head, the acetabular cup, and the backing. Modularity was introduced in hip joint implants to increase mobility, better adjust to the patient’s body, use different materials in one single configuration, and facilitate revision procedure. A junction can be designed between the trunnion and the femoral head, as well as in the femoral neck and stem junction. Nowadays, the model commonly used is a unipolar prosthesis where the trunnion enters a bore in the femoral head, at the junction between the two with several development and advances in designs [3–5].

Modularity leads to surface interactions between parts in relative motion which, in turn, produces wear. Currently, the THA medical procedure has been standardized, and the success rate of the operations has increased over the years. However, wear-accelerated corrosion is still a critical issue that limits the prosthesis’s long-term survival [6]. The corrosion and debris resulting from these tribocorrosion processes (and the effect of the species in the body fluids) are responsible for adverse local tissue reactions, which can lead to health complications in patients. There are differences between degradation on bearing surfaces, which are subject to sliding wear, and on the neck-stem junction, subject to fretting [7]. Indeed, fretting corrosion has been recognized as the main degradation mechanism. However, the appearance of noticeable fretting corrosion depends on several factors, such as the implantation time, impact force during the assembly process, and the length and roughness of the taper [8–14].

Some questions have been raised concerning this issue, such as whether a specific pattern of fretting corrosion exists at the junction; whether a correlation exists between the severity of tribocorrosion phenomena and geometrical construct variables such as neck-shaft angle, stem size, and overall neck length; and whether a correlation exists between the severity of those phenomena and the implantation time. Unfortunately, no method exists to quantify wear-accelerated corrosion in vivo. Moreover, the electrochemical conditions inside the human body affecting the materials in the protheses area unclear, especially those related to the electrochemical conditions and their interaction with mechanical actions. Consequently, some studies have been carried out on explanted implant devices for several years, in order to collect valuable inputs to improve existing devices as well as to develop new models and surfaces [5, 15].

A variety of material combinations are used to manufacture prostheses with high degradation resistance to increase the implant lifespan. Examples include titanium femoral stem – alumina femoral head; Co-Cr femoral stem - Co-Cr femoral head; and stainless-steel femoral stem – stainless steel femoral head. Therefore, it is still unclear if there is a correlation exist between the severity of fretting-corrosion and the tribological pair.

Some studies have been carried out to analyze retrieved surfaces. In 2009, the first retrieval study of a double modular prosthesis made of Co-Cr-Mo alloy was carried out. It was corroborated that long period implantation
results in a high degree of degradation caused by fretting and corrosion phenomena. Debris, holes, and fretting tracks were observed, as were crevice corrosion and intergranular corrosion, although no microstructural abnormalities were observed [8]. De Martino et al. analyzed 60 retrieved prostheses, using modular necks made of a cobalt-chromium alloy and a ceramic femoral head. They found a positive correlation between length of implantation and fretting corrosion scores [7].

Furthermore, a case report of a retrieved Co-Cr neck and titanium stem prosthesis was published in 2015. A severe tissue reaction involving increasing pain and a pseudo-tumor adjacent to the neck-stem junction was associated with fretting-corrosion. Deposits on the neck taper were found, consisting of oxides of cobalt, chromium, and titanium, indicating transfer of titanium from the stem to the neck. In this study, it was also observed that cobalt tends to dissolve while chromium tends to precipitate as oxide [16]. This tribological pair has been demonstrated to be dangerous. In fact, fifteen patients who received this kind of prosthesis for 42.3 months were evaluated along with the retrieved implants; cobalt ion levels measured in all patients were high. Moreover, this study concluded that this system exhibited a high rate of failure related to fretting-corrosion [17]. A similar case was reported where crevices were also observed [18]. Simulations about the degradation level have also been developed. Rodelo-Pantoja et al. [19] reported that under known and expected conditions, the failure is more prone to appear in the neck in any of these materials.

Despite the benefits of modular prostheses, they have disadvantages, including the presence of an additional interface at which fretting corrosion occurs. Particles and ions released because of this tribocorrosion phenomena could be responsible for health complications in patients. Therefore, this work seeks to evaluate three different pairs of explanted stem-neck junctions to analyze the resultant surface. The analyzed trunnions were made of Ti-6Al-4V, Co-Cr, and stainless-steel. Surfaces of explanted trunnions were analyzed in different regions by SEM-EDX and optical profilometry in order to identify degradation mechanisms as well as differences in degradation.

2. Materials and methods

In this study, three kinds of explanted trunnions were analyzed: Ti-6Al-4V, Co-Cr, and stainless-steel. While they were in use, the Ti-6Al-4V trunnion and Co-Cr trunnions were paired to alumina heads. In addition, two kinds of stainless-steel trunnions were analyzed. One of these was paired to a CoCr head and the second to a stainless-steel alloy head. The service times of those prostheses were 1 year for the CoCr trunnion, around 10 years for the 316SS, while the Ti6Al4V trunnion was implanted for 8 years, approximately. All of them were removed because of infection and pain. Once explanted, the hardness of the trunnions was measured at the surface and in the bulk. Also, the chemical composition was determined by means of energy dispersive X-ray (EDX). In order to analyze wear on the trunnion surfaces, a scanning electron microscopy (SEM) was carried out using a Zeiss GEMINI 300 scanning microscope at a high vacuum environment, and optical profilometry was performed. All SEM images were made using an acceleration voltage of 3 kV and a working distance of 6 mm. 3D profiles were taken using a Laser Scanning Confocal Microscope, Keyence VK-X200 Series 3D. Data analysis was developed using the MultiFileAnalyzer 1.3.0.115 software. Figure 1 shows the prostheses under study and the analyzed zones: proximal, distal, and intermediate zones.

3. Results and discussion

3.1 Hardness

Hardness values of the trunnions are shown in Table 1. As expected, surface hardness is higher than bulk hardness, because of the oxide layer. The hardness of CoCr alloy is within the range of hardness reported by A. Lanzutti et al. [20].

<table>
<thead>
<tr>
<th>Material/Zones</th>
<th>Bulk material (HV)</th>
<th>Surface (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V</td>
<td>321 ± 21</td>
<td>358 ± 13</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>632 ± 21</td>
<td>667 ± 31</td>
</tr>
<tr>
<td>CoCr</td>
<td>394 ± 38</td>
<td>400 ± 21</td>
</tr>
</tbody>
</table>
3.2 Surface analysis

In all cases, trunnions showed a thread pattern on the surfaces. These are made to increase the fixation between the femoral heads and trunnions when modular parts are assembled by hammering. EDX, SEM, and profilometry results are shown below. It is worth mentioning that EDX measurements corroborate the chemical composition of the alloys: Ti-6Al-4V and Co-Cr alloys and 316L stainless steel (surgical grade).

Titanium alloys explants

Titanium alloy explant showed the composition indicated in Table 2, and the EDX spectrum is shown in Figure 2. A conventional $\alpha + \beta$ – Ti-6Al-4V alloy was identified [21], even though Fe and Ni are slightly high.

Some debris particles were observed around the deformed material Figure 3 a) - b). Small movements could cause some particles to be trapped in the deformed area. As long as the ploughing generates surface stacking between modular parts, there is less movement, and the ejection of metallic or oxidized worn particles is less likely.

A detailed surface examination shows, deformation marks in the extraction and insertion direction were observed, as shown in Figure 3 c) - d). In this respect, the distal area was the most affected in the areas shown in these images. Furthermore, ploughing on the fillets from the thread was observed Figure 3 e) - g). In arthroplasty procedures, implant parts are assembled by hammering, in order to ensure a tougher fixation between the femoral head and the trunnion. This action produced ploughing in the fillets of the trunnion thread pattern, which suggests an effective stuck phenomenon in the distal area.

Images from the middle part of the trunnion show ploughing, although to a less severe degree than in the distal area. Moreover, some particles of organic material (biofilms), which composition is shown in Table 3 and Figure 4, can be found at this distance, as shown in Figure 3 d). The entry of this material shows that even if the obstruction is produced at the entrance, material and particles can pass through the length of the trunnion.

Furthermore, a closer observation of the smeared areas in Figure 5 shows no cracks or their propagation in distal zones.

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Mg</th>
<th>Si</th>
<th>K</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic %</td>
<td>33.64</td>
<td>13.23</td>
<td>22.20</td>
<td>0.05</td>
<td>1.22</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table 3 Chemical composition of biofilm found in Ti6Al4V trunnion surface (atomic %)

Some differences in material wear were found in the proximal part with respect to the rest of the implant. Nonetheless, ploughing is observed in the thread. Tracks, abrasion lines, and debris particles were also found in the thinner part of the cone, as observed in Figure 6 a) - b). Those findings suggest that more micro-movements were generated in this area, due to the higher wear produced by the fretting mechanism.

CoCr explants

The trunnion made from CoCr alloy was characterized through EDX analysis. The corresponding spectra are shown in Figure 7, and the composition from different parts is indicated in Table 4. According to the literature, the identified composition corresponds to a typical CoCr biomedical alloy [22]. Despite this, elements such as Co, Cr, and C show higher concentrations, which may correspond to material transfer and body fluids. Taking into account that the femoral head was made from CoCr, as the trunnion, the material transfer cannot be successfully identified.

Although the femoral head has a thread pattern to enhance fixation, no significant deformations were observed in the CoCr trunnion as it was observed for titanium alloy explant. This explanted prosthesis shows a large amount of biofilms deposits on the thread pattern fillets in the proximal part (as corroborated by EDX in Table 4). That suggests a free entry of organic matter and its easy deposition in the proximal zone (Figure 8 a, b, and c), suggesting a poor stuck between the trunnion and the femoral head with a mismatch angle as A. Ashkanfar et al. [23] found. Although previous studies [Su et al. [24]] indicate that those deposits are mainly corrosion products, the EDX spectra of the CoCr trunnion analyzed in this study do not show oxygen content. In contrast, carbon content was observed, which suggests that they may correspond to biofilms (Table 4) where the amount of metallic material is more significant. In addition to those layers, deformation lines, such as scratches, as well as detached material in the direction of the insertion and extraction processes (Figure 9 d, e and i) were found in the distal part, and especially in the middle part.

Compared to the titanium alloys prostheses, the deformation level of the thread patterns is lower, and some brittle failures were identified (Figure 9 - 5kX). The latter probably formed during the remotion of the head.
made in the revision procedure. Furthermore, higher hardness, according to Table 1, can explain the lower plastic deformation found (fillet in Figure 8). Moreover, the high dislocation density (produced during fillet machining) could explain the brittle failures observed.
Explanted stainless-steel trunnion against Co/Cr head

The explanted stainless-steel trunnion, as well as the Ti-6Al-4V and CoCr prostheses, are subjected to surface texturization to promote adhesion, as can be seen in Figure 10 a] and cl. The chemical composition by EDX is shown in Table 5, the spectrum shown in Figure 11. SEM images of each part of the trunnion are shown in Figure 10. The distal part exhibits a higher intensity of damage than the proximal part. Tribocorrosion phenomena are evident in the SEM analysis. Abrasion lines are observed along the length of the trunnion and along the direction of insertion and extraction, as well as ploughing in the perpendicular direction of insertion. This is observed in Figure 12. As mentioned, this wear was much lower compared to examined prostheses made of CoCr and Ti6A4V, which could possibly be explained by the stainless-steel hardness (Table 1). However, there is a significant difference in the damage caused with respect to the Ti-6Al-4V prosthesis as, rather than deformed particles; detached particles are observed that are smeared inside the contact and rolled on the surface, creating an abrasive phenomenon, as shown in Figure 13.

Detached particles can be observed in Figure 14. These particles have the same chemical composition as the SS prosthesis. Moreover, no oxygen is observed, which indicates the presence of metallic material. In addition, EDX analysis in Figure 15 shows a material layer formed on the material surface similar to those reported in previous studies [16, 25], [26]. These films, known as a tribofilm, are formed by the oxidized and metallic material worn from both interfaces in contact. The layer was found on the explanted trunnion of 316L stainless steel, which was paired against a Co-Cr alloy head. The alloy contains an average of 18.55% of Cr, according to EDX (see Table 5 and Figure 11). However, the chemical analysis of the surface

**Table 4** Chemical composition of CoCr trunnion surface (atomic %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distal</td>
<td>62.65</td>
<td>32.57</td>
<td>-</td>
<td>0.36</td>
<td>1.07</td>
<td>2.55</td>
<td>0.23</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>Proximal</td>
<td>50.41</td>
<td>24.86</td>
<td>4.34</td>
<td>0.52</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>18.96</td>
</tr>
</tbody>
</table>

**Table 5** Chemical composition of SS surface trunnion (atomic %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic %</td>
<td>18.55</td>
<td>2.22</td>
<td>66.00</td>
<td>13.23</td>
</tr>
</tbody>
</table>
Figure 6 Wear and debris particles found on Ti6Al4V trunnion surface in the proximal zone. Image amplification a) 1000x and b) 3000x

Figure 7 EDX spectra from a) distal part, and b) proximal part of CoCr explanted prosthesis

covered by organic material exhibits higher contents of Cr, of 28.51 %, as well as oxygen contents of 7.33 % (Figure 15). This chromium excess and oxygen could indicate fretting corrosion in this system, with material transfer from the Co-Cr alloy to the SS trunnion.

3.3 Trunnion degradation

Some differences in the degradation level along the trunnion length can be observed from the 3D profilometry maps carried out on the trunnion. Several images along the trunnion length are taken by the confocal and laser microscope and are assembled in order to examine the trunnion extension. The most deformed areas are colored in red. As observed, bigger red zones were localized in the distal than in the middle and proximal region.

Consistent with previous observations in titanium alloy trunnions, the 3D map shows a more extended degradation area in the distal part compared to the proximal part (Figure 16 a)). For the stainless-steel
trunnion, although a difference along the trunnion is observed between proximal and distal zones, it is not as pronounced as in the case of the titanium alloys, as shown in Figure 16 c). Finally, the 3D map taken of the CoCr trunnion shows no significant difference between the distal and the proximal part, as was found in the examination done by SEM.

It is well known that debris and metal particles are found in the tissues surrounding the prosthesis, with adverse reactions. In general, most of the material found has a high content of Cr, rather than Co, due to the tendency of Co to dissolve in the blood. In the case of Ti and CoCr alloys joints, some traces of Co and Ti are found, but the main material is Cr [16, 27, 28]. These indications may correspond to the low deformation exhibited by these particles. Thus, the lower ploughing phenomena in CoCr interfaces favor the particle ejection and the entry of fluids, as observed in this study.

On the other hand, the mismatch angle could make particle ejection arising from the contact between the internal walls of the bore in the femoral head and the trunnion walls more likely. This, in turn, could influence the amount of particles in the surrounding tissue as well as the increase in the metal ions level in the blood.
Figure 10 SEM images of a stainless-steel trunnion from hip explant. Proximal part a) 100x, b) 500x; medium part c) 100x, d) 1000x, e) 5000x; distal part f) 100x, g) 500x

Figure 11 EDX spectrum of SS surface trunnion
Figure 12 Wear mechanisms found in 316L SS trunnion surface

Figure 13 Stainless-steel hip explant degradation, a) 500X and b) 5000X

Figure 14 Detached particles and their chemical composition in SS trunnion surface
In all cases, a degree of ploughing was registered in the distal part as a consequence of the insertion and extraction actions. However, wear caused by fretting corrosion was observed mainly in degradation mechanisms in Ti alloy and SS trunnions.

Titanium alloy ploughing can be explained by the low hardness and the reduced susceptibility of this material to hardening by plastic deformation. However, the extended use of this alloy is supported by its well-known low modulus and stiffness [29]. As detached metallic and oxidized material has similar behavior, the material can be trapped in contacts, smeared, and reincorporated into the material via rubbing on the surface. Although ploughing was found in the thread pattern, a more abrasive performance was observed on the part of the stainless-steel particles rolling in the contact, as shown in Figure 10, which can be explained by the hardness of the material. Once the particle is detached, reincorporating it into the material in the contact can be more difficult compared to what was observed for titanium particles.

Moreover, in all cases, biofilm layers containing material from the alloys and probably, from the organic material in contact with them were identified on the surface. These layers are produced by the tribocorrosion mechanisms taking place on surfaces of the materials in contact, which slide against one another and are in contact with body fluids.
4. Conclusions

- The analysis of retrieved prostheses made from different materials shows the occurrence of tribocorrosion and mechanical degradation on the trunnion surfaces. Dissimilar levels of deterioration were identified between materials and along the trunnion length. More significantly, a high level of ploughing was observed on the thread pattern in the distal part of trunnions made of titanium alloys, which was less severe in those made of stainless steel or CoCr alloy, particularly in the latter. The low material deformation of the CoCr alloy can explain the higher quantity of particles that can be found in systems using CoCr. As the stuck action is not guaranteed by the ploughing, fluids, and material are more prone to enter in and out of contact.
- Differences in the degradation level and mechanisms between the distal and proximal part, especially in the trunnion made of Ti-6Al-4V, suggest bigger movements in the proximal part, given the wear particles found in this area, compared to the ploughing observed in the distal part where the trunnion was probably stuck against the femoral head.
- Those findings imply a significant influence on the mechanical and tribocorrosion degradation of the trunnion on the part of the geometry, mismatch angle, and machining surface, which in turn are amplified by properties of the materials.
- Degradation results should be associated in future studies to clinical data from patients, in order to establish procedures to improve the quality of life of patients.

5. Declaration of competing interest

We declare that we have no significant competing interests, including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

6. Acknowledgments

The authors acknowledge J. Navarro-Laboulais from the Universitat Politècnica de Valencia [Spain] for some of the explants provided for this study.

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