The Fretting Corrosion Resistance of Sol-Gel and PVD Surface Modified Orthopaedic Implant Alloys

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Metallurgy and Materials Science
University of Toronto

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The susceptibility of modular implants to fretting corrosion has raised some concerns as metal ion release and the production of particulate debris may seriously affect implant success, particularly fixation. Two different surface modification techniques were used to deposit thin, hard, wear-resistant, ceramic overlay coatings to Ti6Al4V flats; physical vapour deposition (PVD) and sol-gel thin film processing. In addition, a unique fretting apparatus was designed and constructed.

TiN and ZrN PVD films exhibited an excellent resistance to fretting and appeared well adhered as no evidence of coating failure was observed. The amorphous carbon PVD film was prone to breakdown and the generation of large, deep wear scars. This was thought to be the result of poor film cohesion. The sol-gel-formed ZrO2 coating exhibited large wear scars as a result of substrate failure and the production of ZrO2 coated 3rd body abrasives. Further experimentation with the TiN and ZrN coatings is recommended.
Many people have contributed to this project and I would like to take this opportunity to thank each of them. I would first like to thank Mark Pellman and Multi-Arc Inc. for their support and generous donation of the PVD films on which this study was based. The experimental apparatus could not have been designed and constructed without the help of Chris Pereira and, especially, Dave Abdulla and I would like to thank both of them for their assistance. Special thanks also goes out to Chris for his technical help with the many computer problems I encountered. Mark Filiaggi is to be thanked for his help with the sol-gel thin film processing and his patience with my never-ending questions. Robert Chernecky, Fred Neub, and Sal Boccia all assisted with the scanning electron microscope and special thanks goes out to Robin Tam and the Ontario Laser and Lightwave Research Centre (OLLRC) for their help with the non-contact profilometer. Zirconia film thickness was measured with the help of Lisa Henke at the U of T Erindale campus. I would like to thank my fellow students and friends for their support, especially Siva, Eva Cipera, Peter Kirk, Craig Simmons, Nikki Porter, and Tim Woodfield. Finally, I would like to thank Dr. Pilliar for his guidance and support throughout this project.
# TABLE OF CONTENTS

ABSTRACT ii  
ACKNOWLEDGMENTS iv  
TABLE OF CONTENTS v  
TABLE OF FIGURES viii  
INDEX OF TABLES xi  

## 1.0 INTRODUCTION 1  
### 1.1 ORTHOPAEDIC IMPLANTS 1  
#### 1.1.1 Modularity 1  
#### 1.1.2 Concerns With Modularity 2  
#### 1.1.3 Corrosion of Modular Implants 2  
#### 1.1.4 In Vivo Corrosion Studies 3  
#### 1.1.5 Fretting-Assisted Crevice Corrosion 5  
#### 1.1.6 In Vivo Fretting Corrosion Studies 5  
### 1.2 FRETTING CORROSION 7  
#### 1.2.1 Mechanism of Fretting 7  
#### 1.2.2 Fretting Wear Measurement 8  
#### 1.2.3 Fretting Variables and Wear 9  
#### 1.2.4 In Vitro Fretting Corrosion Studies 14  
#### 1.2.5 Prevention 18  
### 1.3 SURFACE MODIFICATION 18  
#### 1.3.1 Surface Modification Processes 18  
#### 1.3.2 Surface Modification and Fretting 25  
#### 1.3.3 Sol-Gel Thin Films 27  

## 2.0 OBJECTIVES 28  

## 3.0 METHODS AND MATERIALS 29  
### 3.1 MATERIALS 29  
#### 3.1.1 Specimen Preparation 29  
#### 3.1.2 PVD Surface Modification 29  
#### 3.1.3 Zirconia Sol Preparation 30  
#### 3.1.4 Sol-Gel Dip-coating Process 30  
### 3.2 FILM CHARACTERIZATION 32  
#### 3.2.1 Coating Morphology, Thickness, and Structure 32  
#### 3.2.2 Sol-Gel Film Thickness 32  
#### 3.2.3 Chemical Analysis 32
### 3.3 EXPERIMENTAL APPARATUS

3.3.1 Fretting Device: Movement
3.3.2 Fretting Device: Components
3.3.3 Sample Preparation and Test Set-Up
3.3.4 Test Conditions
3.3.5 Single Pass Test

### 3.4 FRETTING WEAR ASSESSMENT

3.4.1 Scanning Electron Microscopy
3.4.2 Non-Contact Optical Profilometry

### 4.0 RESULTS AND DISCUSSION - MATERIAL CHARACTERIZATION

#### 4.1 SURFACE MORPHOLOGY
4.1.1 Roughness
4.1.2 Film Defects

#### 4.2 FILM THICKNESS
4.2.1 Physical Vapour Deposition Films (TiN, ZrN, AC)
4.2.2 Sol-Gel-Formed Zirconia

#### 4.3 FILM MICROSTRUCTURE
4.3.1 Amorphous Carbon
4.3.2 Titanium Nitride (TiN)
4.3.3 Zirconium Nitride (ZrN)

#### 4.4 CHEMICAL COMPOSITION
4.4.1 X-Ray Microanalysis
4.4.2 EDX Linescans
4.4.3 XPS Studies

### 5.0 RESULTS AND DISCUSSION - FRETTING TESTS

#### 5.1 UNMODIFIED Ti6Al4V
5.1.1 Scanning Electron Microscopy
5.1.2 Non-Contact Profilometry
5.1.3 Single Pass Test

#### 5.2 TITANIUM NITRIDE (TiN)
5.2.1 Scanning Electron Microscopy
5.2.2 Non-Contact Profilometry
5.2.3 Single Pass Test

#### 5.3 ZIRCONIUM NITRIDE (ZrN)
5.3.1 Scanning Electron Microscopy
5.3.2 Non-Contact Profilometry
5.3.3 Single Pass Test

#### 5.4 AMORPHOUS CARBON (AC)
5.4.1 Scanning Electron Microscopy
5.4.2 Non-Contact Profilometry
5.4.3 Single-Pass Test
5.5 ZIRCONIUM OXIDE (ZrO₂)
  5.5.1 Scanning Electron Microscopy
  5.5.2 Non-Contact Profilometry
  5.5.3 Single Pass Test

6.0 SUMMARY AND CONCLUSIONS
   (Material Characterization)

6.1 TITANIUM NITRIDE (TiN)
6.2 ZIRCONIUM NITRIDE (ZrN)
6.3 AMORPHOUS CARBON (AC)
6.4 ZIRCONIUM OXIDE (ZrO₂)

7.0 SUMMARY AND CONCLUSIONS
   (Fretting Tests)

7.1 UNMODIFIED Ti6Al4V
7.2 NITRIDE FILMS (TiN and ZrN)
7.3 AMORPHOUS CARBON (AC)
7.4 ZIRCONIUM OXIDE (ZrO₂)
7.5 OVERALL CONCLUSIONS

REFERENCES

8.0 APPENDIX A: POLISHING Ti6Al4V SPECIMENS
9.0 APPENDIX B: ZIRCONIA PRECURSOR SOLUTION
10.0 APPENDIX C: SPECIMEN CLEANING AND PASSIVATING
11.0 APPENDIX D: HANK'S SOLUTION PREPARATION
12.0 APPENDIX E: CONTACT STRESS DERIVATION
13.0 APPENDIX F: ZIRCONIUM OXIDE FILM THICKNESS
# TABLE OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Number of Cycles vs. Volume of Wear Damage</td>
<td>10</td>
</tr>
<tr>
<td>1-2</td>
<td>Normal Load (Pressure) vs. Volume of Wear Damage</td>
<td>11</td>
</tr>
<tr>
<td>1-3</td>
<td>Amplitude of Slip vs. Volume of Wear Damage</td>
<td>11</td>
</tr>
<tr>
<td>1-4</td>
<td>Experimental Set Up, ISO 7206/3</td>
<td>16</td>
</tr>
<tr>
<td>1-5</td>
<td>PVD Cathodic Arc Evaporation System</td>
<td>21</td>
</tr>
<tr>
<td>1-6</td>
<td>Film Growth Modes</td>
<td>22</td>
</tr>
<tr>
<td>1-7</td>
<td>Microstructural Zone Model</td>
<td>23</td>
</tr>
<tr>
<td>1-8</td>
<td>Coating Properties vs. Substrate Bias Voltage</td>
<td>24</td>
</tr>
<tr>
<td>3-1</td>
<td>Dip-Coating Apparatus</td>
<td>31</td>
</tr>
<tr>
<td>3-2</td>
<td>Specimen Clamp</td>
<td>31</td>
</tr>
<tr>
<td>3-3</td>
<td>Central Drive Shaft</td>
<td>33</td>
</tr>
<tr>
<td>3-4</td>
<td>AC Motor with Gear Connection</td>
<td>34</td>
</tr>
<tr>
<td>3-5</td>
<td>CAM/Push-Rod System</td>
<td>34</td>
</tr>
<tr>
<td>3-6</td>
<td>Push-Rod Wedge</td>
<td>35</td>
</tr>
<tr>
<td>3-7</td>
<td>Push-Rod/Wedge/Spring System</td>
<td>35</td>
</tr>
<tr>
<td>3-8</td>
<td>Ti and Co Alloy Specimen Holder</td>
<td>36</td>
</tr>
<tr>
<td>3-9</td>
<td>Bearing Block</td>
<td>37</td>
</tr>
<tr>
<td>3-10</td>
<td>Test Container</td>
<td>37</td>
</tr>
<tr>
<td>3-11</td>
<td>Load Arms/Specimen Container</td>
<td>38</td>
</tr>
<tr>
<td>4-1</td>
<td>High Magnification Image of Amorphous Carbon Film</td>
<td>43</td>
</tr>
<tr>
<td>4-2</td>
<td>Macroparticle Embedded into TiN Film</td>
<td>44</td>
</tr>
<tr>
<td>4-3</td>
<td>Pinhole and Hole in TiN Film</td>
<td>45</td>
</tr>
<tr>
<td>4-4</td>
<td>Large Defect in TiN Film</td>
<td>45</td>
</tr>
<tr>
<td>4-5</td>
<td>Hole in TiN Film</td>
<td>46</td>
</tr>
<tr>
<td>4-6</td>
<td>Cracked Macroparticle Embedded into ZRN Film</td>
<td>46</td>
</tr>
<tr>
<td>4-7</td>
<td>Defect in ZRN Film</td>
<td>47</td>
</tr>
<tr>
<td>4-8</td>
<td>Crack in Sol-Gel-Formed Zirconium Oxide Coating</td>
<td>47</td>
</tr>
<tr>
<td>4-9</td>
<td>Interconnected Cracks in Zirconia Coating’s Edge</td>
<td>48</td>
</tr>
<tr>
<td>4-10</td>
<td>Polished Cross-Section of TiN Coated Disc</td>
<td>49</td>
</tr>
<tr>
<td>4-11</td>
<td>Polished Edge of ZRN Coated Disc</td>
<td>49</td>
</tr>
<tr>
<td>4-12</td>
<td>Polished Cross-Section of AC Coated Disc</td>
<td>50</td>
</tr>
<tr>
<td>4-13</td>
<td>Fractured Edge of Carbon Film</td>
<td>51</td>
</tr>
<tr>
<td>4-14</td>
<td>Fractured AC Film</td>
<td>52</td>
</tr>
</tbody>
</table>
FIGURE 4-15. Fractured Surface of TiN Film
FIGURE 4-16. Fractured Surface of ZrN Film
FIGURE 4-17. ZrN Fractured Surface
FIGURE 4-18. EDX Spectrum of Unmodified Ti6Al4V
FIGURE 4-19. EDX Spectrum of TiN
FIGURE 4-20. EDX Spectrum of ZrN
FIGURE 4-21. EDX Spectrum of AC
FIGURE 4-22. EDX Spectrum of ZrO2
FIGURE 4-23A. Micrograph of TiN Film Used for Linescan
FIGURE 4-23B. Elemental Linescan Across TiN Film
FIGURE 4-24A. Micrograph of ZrN Film Used for Linescan
FIGURE 4-24B. Elemental Linescan Across ZrN Film
FIGURE 4-25A. Micrograph of AC Film Used for Linescan
FIGURE 4-25B. Elemental Linescan Across AC Film
FIGURE 4-26. Relative Atomic % vs. Depth into ZrN Film
FIGURE 4-27. Relative Atomic % vs. Depth into TiN Film
FIGURE 4-28. Relative Atomic % vs. Depth into AC Film

FIGURE 5-1. Fretting Scars on Unmodified Specimen
FIGURE 5-2. High Mag. Image of Unmodified Ti Surface
FIGURE 5-3. Evidence of Material Transfer
FIGURE 5-4. Unmodified Ti Fretting Scar
FIGURE 5-5. Interface Between Damaged and Undamaged Surfaces
FIGURE 5-6. Material Re-Deposited onto Unmodified Surface
FIGURE 5-7. Surface Profiles of Unmodified Ti6Al4V Fretting Scar
FIGURE 5-8. Surface Profiles of Co Sphere Fretted Against Unmodified Ti6Al4V
FIGURE 5-9. Surface Damage Produced From One Fretting Cycle
FIGURE 5-10. High Magnification Image Showing Galling Mechanism
FIGURE 5-11. Fretting Scar on TiN Surface
FIGURE 5-12. Fretting Scar on TiN Surface, Oxide is More Dispersed.
FIGURE 5-13. EDX Mapping of Cr Oxide Debris on TiN Surface
FIGURE 5-14. Fretted Surface of TiN Coated Specimen
FIGURE 5-15. Profiles of Cobalt Counter-Surface Fretted Against TiN
FIGURE 5-16. X and Y Profiles of an Unfretted Co-Alloy Sphere
FIGURE 5-17. ZrN Fretting Scar, Oxide Ring is Less Pronounced
FIGURE 5-18. ZrN Fretting Scar Showing Well-Dispersed Oxide Material
FIGURE 5-19. EDX Mapping of Oxide Debris on ZrN Surface
FIGURE 5-20. Surface Profiles of Fretted ZrN Surface
FIGURE 5-21. COBALT SPHERE FRETTED AGAINST ZrN COATING
FIGURE 5-22. FAILED AMORPHOUS CARBON COATING
FIGURE 5-23. MICROGRAPH OF CENTRAL REGION
FIGURE 5-24. SMALL ‘U’ SHAPED CRACKS PRESENT ON AC SURFACE
FIGURE 5-25. HIGH MAGNIFICATION OF SURFACE CRACK
FIGURE 5-26. MICROSTRUCTURE OF AMORPHOUS CARBON LAYER
FIGURE 5-27. FRETTING SCAR OF THIRD FAILED AC COATING
FIGURE 5-28. EDGE OF FRETTING SCAR SEEN IN 5-27
FIGURE 5-29. FRETTED SURFACE OF AN AC COATING WHICH EXPERIENCED POLISHING WEAR
FIGURE 5-30. PROFILES OF FRETTING SCAR GENERATED ON A AMORPHOUS CARBON COATING
FIGURE 5-31. SURFACE PROFILES OF DEEP FRETTING SCAR PRODUCED ON A AC SURFACE
FIGURE 5-32. SURFACE PROFILES OF AC COATING WHICH EXPERIENCED POLISHING WEAR
FIGURE 5-33. CO SPHERE FRETTED AGAINST AC FILM WHICH EXPERIENCED POLISHING WEAR
FIGURE 5-34. CO SPHERE FRET TED AGAINST AC COATING WHICH FAILED
FIGURE 5-35. LARGE FRETTING SCAR PRODUCED ON ZrO₂ SURFACE
FIGURE 5-36. HEAVILY DAMAGED CENTRAL REGION OF ZrO₂ SCAR
FIGURE 5-37. EDX MAPPING OF OXIDE PARTICLE ON ZrO₂ SURFACE
FIGURE 5-38. SCRATCHES OBSERVED AT THE EDGE OF THE ZrO₂ SCAR
FIGURE 5-39. SURFACE OF ZrO₂ FILM WHICH DIDN’T FAIL
FIGURE 5-40. PROFILES OF A FAILED ZrO₂ SURFACE
FIGURE 5-41. SURFACE PROFILES OF AN UNDAMAGED ZrO₂ COATING
FIGURE 5-42. PROFILES OF CO COUNTER-SURFACE AFTER FRETTING AGAINST ZrO₂
INDEX OF TABLES

TABLE 3-1. HANK'S SOLUTION 39
TABLE 3-2. DISTRIBUTION OF TEST MATERIALS 40

TABLE 4-1. INITIAL SURFACE ROUGHNESS VALUES 42
TABLE 4-2. RELATIVE ATOMIC % OF ELEMENTS IN ZrN FILM 63
TABLE 4-3. RELATIVE ATOMIC % OF ELEMENTS IN TiN FILM 65
TABLE 4-4. RELATIVE ATOMIC % OF ELEMENTS IN AC FILM 66
1.0 INTRODUCTION

1.1 ORTHOPAEDIC IMPLANTS

Total joint replacement has been performed successfully for several decades and prosthetic design has evolved with the development of new alloys, improved understanding of the in vivo environment, new surgical techniques, and different fixation methods. Currently, modular designs are state-of-the-art and afford greater flexibility during surgery, improved fit, optimization of materials, simplified revision surgery, and reduced costs and inventories. Unfortunately, modularity introduces modes of failure not associated with one-piece designs and, consequently, modular implants are prone to enhanced degradation. Modular components are widely used throughout the fields of orthopaedics and dentistry; however, given its preponderance in the literature, this discussion will be limited to the modular hip prosthesis.

1.1.1 Modularity

The concept of modular prostheses was first introduced in 1970 when Harris developed a metal-backed ultra-high molecular weight polyethylene (UHMWPE) acetabular cup. Upon revision surgery, the worn polymeric liner could be replaced without the surgeon having to remove the entire acetabular component. Acceptance of modularity was gradual, however, and it would be more than a decade before modular femoral stems were being designed. In the early 1980’s, the desire for reduced femoral stem stiffness led to the increasing use of titanium alloys (Ti6Al4V) in place of the stiffer cobalt-chrome-molybdenum (CCM) materials.

However, titanium and its alloys possess a poor resistance to wear and abrasion. Characterized by low hardness and high coefficients of friction, these alloys are prone to adhesive galling. During sliding, micro-welding occurs between surface asperities and these contact points are subsequently sheared and plucked away; severely roughened surfaces result. Significant amounts of wear debris generated at the metal-polymer interface would be detrimental to long term implant success and, therefore, wear resistant CCM alloys are preferred for fabrication of femoral head components. Incorporating modularity into their designs, implant manufacturers would be able to improve the wear resistance of the femoral head without increasing the stiffness of the stem. The concern of galvanic and crevice corrosion, however, prevented many manufacturers from doing so.
1.1.2 Concerns With Modularity

Primary concerns in the design and use of modular implants are that wear and corrosion products generated at the modular interface, where the femoral head is press-fitted onto the tapered trunion of the stem, will remain within the crevice and participate as third body abrasives or migrate out of the crevice and interact with the tissues surrounding the implant. Aseptic loosening is the most frequent cause of hip implant failure and is frequently attributed to tissue reaction to wear debris. In such a case, costly and difficult revision surgery must be undertaken. A secondary concern is that surface damage caused by wear and/or corrosion processes may result in areas of stress concentration which, considering the cyclic loading of the hip implant, could promote crack nucleation, propagation, and fracture through fatigue mechanisms.

A study by Chmell et al sought to... "examine the effects modularity may have on the results of total hip arthroplasties (THA) in terms of bone loss, durability of fixation, time to failure, and incidence of revision." Using data from their total joint registry, these researchers reviewed their experiences with THA's done over the last 25 years; comparing patients who differed primarily by the number of modular junctions present in their prostheses. They found that with each incremental increase in modularity there was an earlier appearance of radiolucencies, an earlier occurrence of aseptic loosening, and an increased incidence of osteolysis in the absence of loosening. Chmell concluded that... "suboptimal design rather than the concept of modularity best explains these results."

1.1.3 Corrosion of Modular Implants

The corrosive nature of the in vivo environment was not fully appreciated until the 1930's when fracture fixation plates, made from magnesium and secured with steel screws, were disappearing before the fracture healed. Such examples of the deleterious effects of galvanic corrosion in vivo strongly discouraged the use of dissimilar metals for the construction of surgical implants. Another deterrent was the fact that each modular connection served as a site for both fretting and crevice corrosion. However, recognizing the potential benefits of modular implants, many researchers began investigating the corrosion behaviour of Ti6Al4V/CCM couples.

The electrochemical performance of uncoupled titanium and cobalt alloys was well documented and the general consensus was that these materials possessed excellent corrosion resistance in physiological environments. Researchers such as Hoa and Mears, Mueller, and Solar all reported that titanium and its alloys remained in the passive state even
at potentials above the reversible oxygen potential; suggesting that titanium and its alloys were resistant to static crevice corrosion in vivo. Similar results were obtained for various CCM alloys. This excellent corrosion resistance was attributed to a resilient, protective, passive oxide layer present on the alloy’s surface. Although encouraging, these results were for uncoupled scenarios and did not address the phenomenon of galvanic corrosion.

One of the earliest investigations into the coupling of orthopaedic implant alloys was performed in 1975 by Kummer et al. ⁹ who concluded that the cobalt/titanium couple was stable and unlikely to experience any enhanced corrosion in an isotonic saline solution. Likewise, Griffin et al. ¹⁰ concluded that ... “the relative corrosion resistance predicted for the couple between Ti6Al4V and CCM (in saline) indicated that no detrimental changes due to galvanic effects are expected.” Other researchers ¹³,¹⁴ validated these results and all agreed that great care must be taken when combining metals in vivo.

1.1.4 In Vivo Corrosion Studies

Once the concerns of galvanic and crevice corrosion had been expelled, production and routine implantation of modular prostheses followed. Initially, these implant systems enjoyed a tremendous amount of clinical success. Recently, however, investigators ¹²,¹⁵,¹⁷,¹⁹,²⁰,²⁴ examining retrieved hip implants have reported signs of excessive degradation at the modular interface between the femoral head and stem components. Several degradation processes not associated with one-piece implants, namely crevice corrosion, galvanic corrosion, and fretting were thought to be responsible.

A 1991 study by Collier et al. ²² investigated 88 uncemented, porous coated femoral hip implants and observed corrosion in 56.6% of the mixed alloy designs. No corrosion was observed for the all-cobalt or all-titanium modular implants. Corrosion was commonly found on both components and examination with the SEM revealed severely pitted surfaces; characteristic evidence of crevice corrosion. In fact, these researchers attributed the damage to accelerated crevice corrosion and suggested that the... “corrosion observed in this study required a dissimilar metal combination, breakdown of the passive film, and body fluid in the taper between the two components.”

Collier suggested that the main driving force behind this reaction was the galvanic corrosion potential between the two alloys even though coupling of these alloys in vivo was predicted to be safe. The lack of corrosion on the single alloy designs and the large percentage of corroded mixed metal implants was unquestionably the foundation of Collier’s theory, however, reports of corrosion on both components questions the presence of a galvanic corrosion effect.
A subsequent study by these same researchers investigated 139 modular femoral prostheses and reported evidence of corrosion in 52% of the mixed alloy systems. Again, no corrosion was observed for the single alloy implants and scanning electron microscopy revealed severely pitted surfaces on both the cobalt and titanium components. Stereoscopic examination of all implants failed to find any evidence of fretting.

Once again, Collier attributed this degradation to galvanically-accelerated crevice corrosion and ruled out any contribution due to fretting, because:
1. Corrosion was observed in mixed metal prostheses only.
2. Scanning electron microscopy showed deep pits characteristic of crevice corrosion.
3. The harder cobalt surfaces, which would be expected to suffer less damage when fretted against the softer titanium alloys, experienced more material loss.
4. Fretting corrosion requires an oxidizing environment (see Sec 1.2.1) and the crevice environment between the femoral head and stem is depleted in oxygen.

Collier suggested that the passive films may be destroyed during implantation when the harder CCM femoral head is press fitted onto the Ti alloy stem. While there is no question that surface damage may occur during assembly, it must be remembered that at that time, no body fluids are entrapped within the crevice and there is no reason for the crevice to be depleted in oxygen; therefore, repassivation would still be possible. The occurrence of corrosion on both components, once again, questions this galvanically accelerated crevice corrosion theory and one wonders if examination with a low mag (60X) stereoscope is sufficient enough to view surface damage produced by fretting at the micron level.

Mathiesen et al examined nine uncemented, Co/Co modular hip prosthesis which had been revised because of infection, loosening or fracture, loosening of threaded cups, and protrusion of bipolar cups. Mathiesen found tissue discolouration and macroscopic corrosion in four of the nine prostheses. The corrosion was located at the head/neck junction and, in most cases, histological examination showed extensive necrosis associated with metallic particles. Mathiesen reported the presence of porosity and chemical inhomogeneity close to the head/neck interface and noted that no scratches, or marks indicative of relative movement between the two components, were found. Based on these observations, and the fact that the femoral heads were tight and had to be removed with tools, Mathiesen concluded that the degradation experienced by the four implants was the result of crevice corrosion, facilitated by structural imperfections.
However, fretting cannot be excluded simply by the fact that the two components were well fixed and had to be removed with tools. Fretting corrosion has been known to occur at slip amplitudes smaller than 1 micron and components which appear 'well-fixed' could certainly be experiencing relative movement on the micron scale. In fact, if the femoral head was noticeably loose, the fretting regime would have most likely been passed and the two components would be experiencing reciprocating sliding wear. Like Collier, Mathiesen's examination techniques may have been insufficient to identify any damage caused by fretting.

1.1.5 Fretting-Assisted Crevice Corrosion

With a few exceptions, the majority of researchers support the theory that this enhanced degradation is a result of the breakdown of the passive films and the development of an unstable electrochemical environment within the crevice. Breakdown of the films could occur if the femoral head and stem components experienced slight relative micro-movement, known as fretting. The first half of the fretting cycle would destroy the passive films exposing bare, unreacted metal. Repassivation would occur almost instantaneously and this newly formed film would be removed, subsequently, on the return half cycle. This process of film removal and formation would continue until the crevice became depleted in oxygen, at which point repassivation would no longer be possible. Within the crevice, the pH level would drop and with the bare, unprotected metal exposed, crevice corrosion would proceed.

Wear debris and corrosion products generated by the fretting action could act as abrasive particles and contribute to third body wear both within the crevice and/or at other articulating surfaces. The wear debris could also migrate out of the crevice and interact with the tissues surrounding the implant inducing an undesirable biological response such as bone resorption.

1.1.6 In Vivo Fretting Corrosion Studies

Collier's 1995 study examined 651 femoral hip prostheses, 411 of which were modular and 240 of which were one-piece designs, for fretting, corrosion, and wear. Corrosion was observed in more than 35% of mixed metal modular designs, less than 10% of the all-Ti alloy components, and in less than 6% of the all-Co alloy prostheses. Of the 53 mixed metal modular prostheses which were corroded, 3 showed evidence of fretting. Surprisingly, of the 92 non-corroded mixed alloy prostheses, 8 had significant in vivo fretting. Although none of the all-titanium modular implants which experienced corrosion
showed any signs of significant fretting, 10% of those which were not corroded did. Only
one incidence of fretting was found for the all-cobalt modular implants and it occurred on a
corroded prosthesis. Collier's study also investigated other common modular connections
and found evidence of fretting in 50% of snap-fit collars, 38% of modular sleeves, and
21% of bullet tips.

Collier stated that severe fretting between the head and neck tapers was
accompanied by significant corrosion and admitted that ... "as fretting and the associated
loss of metal can occur as the result of relative micromotion in the micron range, more
metal loss may be in process than is easily observable with the dissecting microscope (10-
63X) typically used by the authors." Collier concluded that factors accelerating the rate of
corrosion included breakdown of the passive films, either during impaction or subsequent
fretting, heterogeneity of the implant alloys, and taper configurations which allow the
intrusion of the aqueous environment. There was no mention of galvanic corrosion.

Gilbert et al examined 148 modular hip prostheses both of mixed (Co/Ti) and
similar (Co/Co) metal combinations. Using optical microscopy, SEM, and energy
dispersive X-ray analysis (EDXA) these researchers observed significant corrosion on both
components for each implant system. In fact, Gilbert identified several forms of corrosion
including etching, fretting, pitting, selective leaching, and intergranular attack. Fretting
was identified by the removal of machining marks and the presence of a roughened surface.
Examination with the SEM revealed regions where the Co-Cr material had been transferred
to the Ti-alloy neck and remained attached to the neck after the two components were
separated. Gilbert believed that the mechanism responsible for the enhanced degradation
observed in this study was fretting-assisted crevice corrosion and because this theory has
been previously discussed, it will not be presented here.

A 1993 study by Cook et al examined 108 uncemented, porous coated modular
femoral stems which had been removed for reasons other than loosening. These
researchers reported mild to moderate corrosion in 34.5% of mixed alloy systems, in 7% of
the all-cobalt systems, and in 67% of the all-titanium implants. It should be noted that only
three all-titanium implants were examined and no evidence of severe corrosion was
reported for any implant system. Contrary to Collier and Gilbert, these researchers reported
no correlation between the presence of corrosion and time in situ. Another important
observation by Cook was that implants which showed signs of corrosion were less likely
to have bony ingrowth. Cook suggested that the... "most likely clinical sequence of events
is fretting leading to the breaching of the passive layer of the alloy surfaces followed by a combination of crevice and galvanic corrosion.”

1.2 FRETTING CORROSION

Fretting corrosion occurs in situations where two surfaces are in contact permanently, such as: press fitted hubs, riveted joints, bolted joints, and also in contacts which are only at rest for short periods of time, ball and roller bearings for example. It is defined as “the forms of damage which arise when two surfaces in contact and nominally at rest with respect to each other, experience slight periodic relative movement.” The debris produced from fretting is usually an oxide and because its volume is often greater than the metal from which it is formed, the type of contact becomes important.

If the debris cannot escape from the fretting region then an increase in pressure may result. In the fixed type of contact this is usually not a concern, except for the case of steel ropes where fretting damage between the individual cables may force them apart and form a bulge on the exterior of the rope. For occasionally moving contacts, entrapped debris may lead to seizure. If the fretting debris can escape the contact area it results in a loss of fit between the surfaces and a decrease in clamping pressure which, in turn, may lead to greater vibration. In machinery, escaping debris may migrate to other components and serve as third body abrasives, causing further wear problems.

Another important concern with fretting corrosion is the ensuing surface damage. Cracks generated near the edge of the fretting region may act as stress concentrators and component fracture attributable to fatigue processes is possible.

1.2.1 Mechanism of Fretting

Over the years several theories attempting to explain the mechanism of fretting have been proposed. Observing surface damage on hard materials in a short period of time under conditions of small slip and almost no load, researchers Tomlinson, Thorpe, and Gough rejected the idea of fretting being an abrasive process and concluded that the damage was the result of molecular attrition. In this theory it was suggested that the two surfaces approached each other so closely that the force fields of the surface atoms overlapped. Fretting damage was considered to be a result of atoms being plucked from each surface; this theory has generally been rejected.

During their fretting studies, Oding and Ivanova found a thermoelectric effect and claimed that there was an electro-erosive action associated with it. Similar to the above theory, these researchers suggested that surface atoms were ripped from the material which
was anodic to the other. Atoms moving in to fill the vacant sites at the surface lead to the migration of vacancies into the region below the surface. This continues until the concentration of vacancies reaches a critical value and they precipitate as micro-pores or micro-cracks. This theory implies that a noble metal, such as copper, would be extremely damaging when fretted against steel; however, this is not the case and this theory has also been widely rejected.

Current theories \(^\text{46}\) are that the damage is caused on a larger scale and there seem to be three basic processes:

1. Sliding of one body over another disrupts the oxide films present on both surfaces and exposes clean and possibly strained metal. The metal surfaces may be very reactive and in the presence of an atmosphere would oxidize rapidly during the first half cycle after the disruption, only to be re-disrupted on the return half cycle.

2. Metal particles are removed from the surface by a mechanical grinding action or by the formation of welds which are subsequently broken, either by direct shearing or by a local fatiguing action. The atmosphere would play no part in this process except where fatiguing was involved.

3. Oxide debris resulting directly from (1) or as a result of the oxidation of the metal particles in (2) acts as an abrasive powder which continues to damage the surfaces.

All three of these processes occur and their relative importance depends on several fretting variables, such as atmosphere, ability of the materials to work harden, load, and geometry.

1.2.2 Fretting Wear Measurement

The damage resulting from any type of wear test is often quantified by determining the volume of material removed from the test specimens. There are several approaches which can be taken and the methods used are often determined by the geometry of the test specimens, the test environment, and the type of wear. Commonly used techniques include measuring the size and depth of the wear scar, determining the amount of wear debris, or calculating the weight loss of the test specimens.

Volume calculation through wear scar measurement is an effective method provided that the wear scar is of reasonable size and has a relatively uniform shape. If the wear scar is sufficiently large, a profilometer can be used to trace out its vertical profile; successive parallel traces produce a 3-D contour map of the scar. A profilometer is an instrument in which a small diamond stylus is dragged across the specimen’s surface, much like the needle on a record player, and the resulting vertical fluctuations of the stylus are amplified and recorded on graph paper. However, if the material being examined is very soft, like
titanium, the diamond needle may plough through the material instead of riding on its surface. Another limitation to this method is that the diamond stylus may be too large to enter and trace out the actual shape of very small holes or pits.

These problems have been overcome, to an extent, with the development of non-contact optical profilometers. These instruments use white light interferometry to produce 3-D relief maps of a surface and can obtain a vertical scanning resolution as high as a few nanometers. The advantages of non-contact profilometry include increased resolution, increased speed, the ability to examine delicate surfaces, and the ease of making volume, area, and step measurement calculations. The disadvantage of both profilometer techniques is that the geometry of the test specimens must be relatively simple.

Volume measurements can also be accomplished by collecting and weighing the particulate wear debris. Filters are often used to facilitate debris collection, however, and there is always a chance that very small particles could be excluded. If a significant amount of the debris was within this particle size range, volume calculations could be considerably affected. Corrosion and oxidization of the wear debris is also a concern as these processes can alter the particle’s size, chemistry, and morphology.

The most common method used to quantify wear damage is to calculate the weight loss of the test specimens. In this method, the test components are weighed on a micro-balance before and after the test. As with the analysis of the debris particles, the weight loss of the specimens, combined with the density of the material, can be used to calculate the volume of material removed. The main advantage of this technique is that test specimens of complex geometries can be easily measured. If the wear volume is very small however, the weight loss of the components may be within the experimental error of measurement and the resulting wear volume measurements would be unreliable. In many wear tests, material transfer from one specimen to the other is common and, in this case, weight loss measurements would not give a true indication of the damage done.

1.2.3 Fretting Variables and Wear

There are several factors which can affect the extent of damage and these variables can be divided into three groups. The first group includes the mechanical variables such as number of cycles, normal load, amplitude of slip, and frequency. The second group are physical variables such as temperature, surface roughness, and relative hardness of the surfaces. The final group includes variables such as composition of the atmosphere, humidity, and liquid lubricants which influence the chemical processes occurring.
Mechanical Variables

In most fretting studies on steel, the volume of material removed is proportional to the number of cycles. Initially, there is a high rate of wear associated with a ‘running-in’ period, however, the curve eventually becomes linear (Fig 1-1). Examination of the first few hundred fretting cycles prompted Feng and Rightmire \(^{54}\) to suggest that this ‘running-in’ period consisted of three stages (not shown). The initial rapid weight loss is due to the removal of oxide films which result in the generation of loose particles. Contact areas void of oxide then experience simultaneous material loss and gain and as a result, the rate of weight loss is lower. As more areas of contact are developed, plastic deformation at each contact point is reduced and material transfer tends to fall off; loose particles are again generated and the rate of wear increases.

![Figure 1-1. Relationship between number of cycles and fretting wear volume for steel in various atmospheres. (46)](image)

For flat steel surfaces, the volume of fretting damage increases linearly with increasing normal load, provided that the amplitude of slip is held constant (Fig 1-2). If the increase in normal load causes a reduction in the slip amplitude, the two factors work against each other and the damage first increases, passes through a maximum, and then decreases.

The effect slip amplitude has on the fretting damage is dependent upon the contact geometry. For flat steel surfaces in dry air, the volume of material removed increases linearly with increasing amplitude of slip. Unfortunately, for other geometries the relationship is not so simple. For the case of rotational oscillation of a cylinder against a
flat, the relationship between slip and the volume of material removed can be seen in figure 1-3. This curve suggests that there is a limiting slip amplitude below which the fretting damage is insignificant. Tests done on the same machine reveal that, although different combinations of materials produce similar shaped curves, the limiting value of slip varies for each couple.

![Graph showing relationship between normal load (pressure) and fretting wear volume for a flat-on-flat configuration.](image)

**Figure 1-2. Relationship between normal load (pressure) and fretting wear volume for a flat-on-flat configuration.** (46)

![Graph showing relationship between amplitude of slip and fretting wear volume for a cylinder on flat configuration.](image)

**Figure 1-3. Relationship between amplitude of slip and fretting wear volume for a cylinder on flat configuration.** (46)
Physical Variables

Although it is widely known that the rate of corrosion increases with increasing temperature, the effect temperature has on fretting corrosion is quite different. It has been discovered that the fretting damage is more severe at lower temperatures (< 273 K) and although this may be connected to the brittle-ductile transition temperature, it is more likely associated with the reduced effectiveness of adsorbed moisture as a liquid lubricant. Studies reveal that between 348 K and 423 K the fretting damage appears to be constant. The disruption of thicker oxide films, produced from increased oxidation rates at higher temperatures, should lead to an increase in fretting wear; however, some results indicate that this is not always so. Wright discovered that on surfaces with a good finish there is a transition temperature at which the wear resistance suddenly increases. This improved performance has been attributed to the development of an adherent, protective, oxide film which acts as a solid lubricant between the two contacting surfaces. However, if the fretting is severe or the oxide film doesn’t possess the mechanical properties to avoid breakdown, the resulting wear will be more severe than at lower temperatures because of the enhanced rate of oxidation.

Hardness is one of the key material properties in terms of fretting wear resistance; influencing the fretting behaviour in two ways. Firstly, a higher hardness implies higher yield and higher fatigue strengths. Since fretting damage involves surface breakdown by local high stress fatigue processes, a higher hardness implies a greater resistance to surface damage. Secondly, harder surfaces possess a greater resistance to abrasion and, therefore, third body oxide particles generated through the fretting action will be less destructive.

Surface roughness plays an important role in fretting wear and its effect may be somewhat unexpected. It is well known that the higher the degree of surface finish the more serious the fretting damage. On rough surfaces the debris generated through the fretting action will have a better chance of escaping the areas of contact and accumulating in the hollows between the asperities. This reduces the effect of the wear particles as third body abrasives. Further, work hardening will likely prevent the asperities from being completely flattened and, therefore, the sharper asperities on rough surfaces will be able to take up more of the tangential movement by elastic deformation. Surprisingly, at elevated temperatures the effect of surface finish is reversed; this is thought to be the result of a less adherent oxide film.
Environmental Variables

The environmental variables, including composition of atmosphere, humidity, and lubrication, are extremely important in determining the extent of the fretting damage. A variation in the concentration of corrosive agents within the environment is expected to have an effect on the volume and nature of the fretting debris. Studies investigating the effects of the fretting environment report that, for steel and aluminum, the resulting surface damage is the same for fretting in air and in oxygen. However, fretting in a vacuum significantly reduces the amount of surface damage. Fretting in a protective atmosphere, such as nitrogen or helium, reduces the damage measured as weight loss but considerable surface roughening occurs. This is due to material being transferred from one surface to the other with the production of very few loose particles.

Tissue reaction to particulate debris is important to implant success and therefore, the interaction of wear debris with the surrounding environment is of great interest. Shahgaldi et al \(^{11}\) reported that the chemical composition of wear particles embedded in the soft tissues around orthopaedic implants was different from the alloys from which they were generated. Using CCM and Ti6Al4V alloys, they found that the debris contained small amounts of titanium and cobalt but consisted mostly of aluminum and chromium. It was also reported that there was a widespread giant cell reaction to these particles. These results indicate that corrosion is continually altering the shape, size, and composition of the implanted alloy and a tissue environment favouring bone resorption may result.

Humidity has very little effect on the fretting damage in a protective atmosphere but has a great influence when oxygen is present. Generally, the damage decreases linearly with increasing humidity. This effect can be explained as follows: water adsorbed on the surface of debris particles acts as a lubricant. As the humidity is increased, the debris can disperse more readily from original points of formation. At very low humidity, the debris is not dispersed and the production of debris continues at the same initial points leading to the formation of deep pits.

Lubricants can influence the fretting process in three ways:
1. Restricting the access of oxygen to the fretting region.
2. Sweeping away abrasive debris particles.
3. Altering the coefficient of friction.

As mentioned above, the addition of oxygen plays an important role in fretting and limiting the amount of oxygen present at the fretting site can significantly decrease the surface damage. Flowing lubricants improve the fretting resistance by removing the abrasive
component of fretting. Particles which would otherwise act as third body abrasives are removed from the fretting site as quickly as they are generated. Finally, reducing the coefficient of friction lowers both the frictional forces present and the resulting shear stresses.

1.2.4 In Vitro Fretting Corrosion Studies

Although there have been numerous studies investigating the fretting behaviour of orthopaedic alloys, no standard fretting corrosion test exists for modular implants. Consequently, researchers design and construct their own experimental apparatus or make use of other standards not intended for modular implants. This results in a wide range of testing conditions and variables, such as specimen geometry, loading, testing environment, frequency, duration, amplitude of slip, and temperature. Also, various techniques have been used to quantify the fretting damage, namely optical and scanning electron microscopy, weight loss measurements, energy dispersive x-ray spectroscopy (EDX), profilometry, and atomic absorption spectrophotometry. This wide range of testing conditions and the numerous techniques used to quantify the damage make comparing these studies difficult. Rarely can numbers be compared from study to study.

Several studies employ ASTM F-897 in an attempt to characterize the fretting corrosion of orthopaedic alloys. Entitled “Standard test method for fretting corrosion of osteosynthesis plates and screws”, the test consists of a two hole plate through which cortical bone screws are fastened to Delrin posts. The fretting motion between the screw heads and the plate countersinks is produced by rocking the Delrin rods back and forth. The materials tested in these studies included 316L stainless steel, MP35N, Ti6Al4V, and wrought CCM. Some studies tested mixed metal combinations, while others investigated single alloy fretting. Testing conditions and environments varied significantly. Normal loads ranged from 65 N to 500 N, the number of cycles ranged from 259,200 to 1,209,600, and the testing environments included saline (0.9% NaCl), saline plus 10% fetal calf serum, and RPMI 1640 tissue culture medium with varying concentrations of CaCl2 and H2O2. Finally, all tests were performed at ambient temperatures with a frequency equal to 1 Hz.

The study by Kawalec and Brown was particularly relevant to modular hip prostheses because it used the common orthopaedic alloys, Ti6Al4V and wrought CCM. Different combinations of these alloys were fretted for 1.2 million cycles in a saline plus 10% fetal calf serum solution with a maximum relative motion of approximately 120 μm. Although this displacement is somewhat high (the relative micromotion expected between
well-fixed modular components is between 10-25 μm) \textsuperscript{37} it is still within the accepted fretting range. This study reported a total weight loss of 4570 μg when Ti was fretted against itself and a loss of 620 μg and 3860 μg when Ti was fretted against CCM screws and plates, respectively. The large wear of the Ti/Ti couple was a result of titanium’s susceptibility to adhesive galling and in all cases the screws lost more weight than the plates.

The screws’ increased susceptibility to fretting corrosion was a consequence of the testing apparatus. As Kawalec states... "as the screw rocks back and forth in the countersink, it slides over the abrupt edge of the countersink, resulting in increased damage to the screw head." Besides significantly reducing the damage caused by fretting, \textsuperscript{31,32} the addition of 10% calf serum to a saline solution more closely simulates the extracellular environment in vivo. Consequently, in vitro tests conducted in such a solution should be more relevant. However, Kawalec and Brown countered this by performing their tests at ambient temperatures; suppressing one of the key variables which affects the rate of corrosion.

Other researchers\textsuperscript{25,28,30} investigating the fretting corrosion resistance of modular implants chose to adopt a test which used actual implants. These tests, based on the ISO standard for assessment of fatigue strength of hip stems (ISO 7206/3:1991), involves securing the femoral stem in acrylic cement and applying a cyclic fatigue load to the femoral ball in the appropriate orientation. (Fig 1-4)

To our knowledge, no studies have been performed which attempt to determine the frequency of movement and, more importantly, the contact stresses present within the modular head/neck junction. As a consequence, in vitro studies use a wide variety of stress levels and, as mentioned previously, comparing results from different studies can be difficult. Furthermore, the relevance of each study is unknown. The advantage of using actual implants is that the loads exerted on these devices are well documented\textsuperscript{37,39} and the appropriate contact stresses will arise as if in vivo. Disadvantages of using actual implants include cost, reliability of test specimens (roughness, tolerance, etc.), and complex geometries.
Figure 1-4. Experimental set up, in accordance with the ISO 7206/3 standard.

As with the tests based on ASTM F-897, the three tests based on ISO 7206/3 used a wide variety of testing conditions. Frequencies ranged from 0.6 to 10 Hz, number of cycles varied between 1 million and 20 million, and loads used ranged from 200 and 4200 N. Two studies were performed at ambient temperatures while the third chose to simulate in vivo conditions and tested at body temperature, 37 °C. The testing solutions used in these studies included air, Ringer's solution, FeCl₃, and a 0.9% saline solution.

The purpose of the study by Flemming et al was to develop a test which could be used to study the fretting corrosion at the head/taper interface; this was accomplished by monitoring the fretting current. Their results suggested that... “the taper angle could have more of an effect on the fretting corrosion than the head-neck extension. A smaller taper diameter could result in more bending of the taper during loading and more relative movement.”

The two studies by Viceconti et al, which investigated the fretting corrosion of modular implants differing in design, reached similar conclusions. One study compared the differences between commercial and prototype implants, whereas the other investigated
the effects of stem size. Both papers concluded that fretting could be minimized or eliminated with accurately designed taper fittings. Further, Viceconti suggested that throughout one million load cycles, which is estimated to be the yearly load history, the amount of debris generated at the modular head/neck interface would be approximately 0.6 mg. Suggesting that a normal and stable prosthesis was likely to produce less than 10 mg/yr., Viceconti questioned the significance of another 0.6 mg.

Another option for researchers investigating the fretting corrosion of modular prostheses is to construct their own fretting apparatus. Bhambri et al. did this by mating actual femoral heads to simulated taper cones. These tests were carried out in Ringer’s solution at 37 °C for 10 million cycles with a fatigue load equal to 5.34 KN. Two femoral heads were tested, one made from a CCM alloy and the other from alumina, and both were mounted on Ti6Al4V stems. Part of the stem was thermally nitrided to form a ceramic layer of TiN on the surface. The load was applied to the head at 30°, simulating a 15° mediolateral anatomic orientation. The non-nitrided Ti6Al4V surface mated against CCM showed signs of fretting and material transfer from the stem to the head, while the nitrided parts exhibited minimal changes in surface topography and little material transfer. No significant fretting damage occurred to either the nitrided or non-nitrided Ti6Al4V surface when fretted against alumina.

Finally, Cook et al. used a cylinder on flat configuration to investigate the effect of number of cycles and solution on the behaviour of various orthopaedic alloys fretted against themselves. Using CCM, 316L, and Ti6Al4V, it was shown that weight loss increased with the number of fretting cycles but then reached a plateau where further weight loss was negligible. It was observed that 316L lost more weight than CCM at any number of cycles. These authors also reported that the weight loss of the titanium alloy was similar to that of the cobalt based alloy, although the titanium surfaces exhibited more abrasion. The addition of 0.5 % albumin to the saline solution resulted in marked decrease in weight loss for all of the alloys. Except for CCM fretted in the saline plus albumin solution, all samples exhibited scratches which, under microscopic examination, proved to be large grooves dug into the surface caused by the proud parts of the opposing surfaces.

Although the frequency used was 6.25 Hz, the surface stress was equivalent to 1.2 MPa, and the amplitude of slip was maintained at approximately 20 μm, the relevance of this test to the fretting corrosion resistance of modular hip implants has to be questioned as no mixed metal fretting was investigated and all tests were conducted at ambient temperatures.
1.2.5 Prevention

Many of the studies discussed in the previous section suggest that the fretting corrosion problem can be reduced or eliminated through improved taper design and manufacturing tolerances. In fact, a study by Shareef and Levine\textsuperscript{37} investigated the effects manufacturing tolerances had on the micromotion at the head/neck taper using the finite element technique. These authors suggested that control of the tolerances of both components could minimize both the micromotion and the contact stresses present at the modular interface. They concluded that the magnitude of the micromotion was sensitive to manufacturing tolerances on the stem taper; changes to the femoral head taper were not investigated. An increase in manufacturing tolerances is accompanied with an increase in manufacturing costs however, and, furthermore, increasing tolerances does nothing to protect the alloys should relative micromovement develop.

Another solution to the fretting problem is to modify the surface properties of one or both of the alloys involved. This can be done using various surface modification techniques which alter key surface properties such as wear resistance, corrosion resistance, and hardness, without altering the bulk properties of the material. Depending on the process, hard, wear-resistant ceramic materials can be deposited onto the surface as either a diffusion layer or an overlay coating. In fact, surface modification may represent the more attractive solution as it could be used to protect other components which commonly experience fretting, such as femoral stems, acetabular components, knee implants, and fracture fixation plates.

1.3 SURFACE MODIFICATION

While their mechanical and chemical properties make titanium and its alloys acceptable implant materials, their resistance to adhesive and abrasive wear is poor. Various surface modification techniques can be used to apply a thin, hard, wear resistant, and biocompatible coatings, such as TiN, to the alloy’s surface without significantly affecting key properties such as fatigue strength, yield strength, and stiffness. Widely used surface modification techniques include chemical vapour deposition, physical vapour deposition, nitriding, and ion implantation.

Coating performance depends on coating properties such as adhesion, abrasion resistance, surface roughness, residual stresses, uniformity, and defect density. These properties are significantly influenced by the microstructure which is controlled by several process parameters including temperature, time, and pressure.
1.3.1 Surface Modification Processes

Chemical vapour deposition (CVD) uses chemical reactions between vapour phase reagents to form thin coatings on heated substrates. The process starts with a gaseous reactant and the CVD chemical reaction, commonly a reduction reaction, takes place on the surface of the substrate. Reduction reactions are important because in the presence of another reactant gas, compounds such as TiN may be deposited. Deposition is favoured by reduced pressure and the process for depositing titanium nitride films is as follows:

\[
\text{TiCl}_4(g) + 2\text{H}_2(g) + \frac{1}{2}\text{N}_2(g) = \text{TiN}(s) + 4\text{HCl}(g)
\]

The CVD process has the advantage of being a near equilibrium process which makes it possible to choose a set of deposition parameters (temperature, pressure, reactant concentration, and gas stream velocity) and attain a reasonably predictable coating composition. The CVD process is applicable to a wide variety of materials and because it is not a line-of-sight process, uniformly thick coatings can be applied to complex shapes. This process also has the ability to coat large objects. Disadvantages of the CVD process include low deposition rates (0.1-0.001 mm/hr) and relatively high processing temperatures (>600 °C). This high temperature requirement virtually eliminates plastics and die-cast alloys from being coated by CVD. The applications for CVD coatings are numerous; however, these coatings find greatest use in fabrication of microelectronic devices and in the production of tools and machine parts for metal cutting and forming.

Ion nitriding is a surface reaction which uses a glow discharge to chemically combine nitrogen with the elements of the substrate. The component to be coated is placed inside a vacuum chamber which is subsequently evacuated and then backfilled with a mixture of nitrogen and hydrogen. The presence of hydrogen insures that the surface of the metal is oxide free, permitting the nitrogen ions to diffuse rapidly into the substrate. During ion nitriding, the temperature of the substrate increases as a result of ion bombardment. Some advantages ion nitriding has over conventional gas nitriding include shorter treatment times, continuous surface cleaning, less distortion, and a pollution-free environment.

Nitrogen ion implantation is a physical process in which nitrogen ions are driven into the surface of a metal and remain within the lattice as discrete atoms. The process is carried out at low partial pressures and the substrate temperature must be kept low in order to avoid surface chemical reactions which could result in ion nitriding effects. In this
process, a gun generates nitrogen ions and accelerates them towards the substrate with enough energy to penetrate the surface and come to rest at suitable sites. The depth of penetration is very shallow (0.05-0.3 μm) compared to other surface modification techniques. This process is usually used to improve wear resistance but there are reports that ion implantation significantly improves rotating bending and vibrational fatigue life.

Physical vapour deposition (PVD) is a generic term which is used for any coating process involving the deposition of physically generated atoms onto a surface in a vacuum environment. There are three fundamental PVD processes including evaporation, sputtering, and ion plating and each has numerous variations. There are however, several features and requirements which are common to all processes, these include:
1. A high vacuum system with low impurity gas levels and the ability to introduce controlled flow rates of several working gases.
2. A substrate mounting system which controls substrate temperature and orientation within the vacuum chamber.
3. Coating materials with a well controlled vapour flux.
4. Carefully prepared and reproducible substrate surfaces.
Many PVD processes have additional requirements such as the introduction of reactive gases or the application of a substrate bias voltage.

PVD processes are the most widely used coating methods and evaporation and sputtering are currently the most widely applied forms of PVD. Deposition rates as high as 0.07 mm/min can be achieved and these coatings find applications in microelectronics, circuit fabrication, control of light reflectance/absorption, corrosion/oxidation mitigation, decorative coatings, and tribology. PVD fabricated materials include metals and metallic alloys, ceramic compounds, metal/ceramic and metal/polymer layered composites, and semiconductors. Suitable substrates range from metals to ceramics to polymers and a wide variety of industries use PVD technologies in their products and manufacturing processes.

Evaporated films, first developed by resistance heating in the late 1800’s, are deposited through a process which involves the heating of a source material to a sufficiently high temperature, usually in a high vacuum environment. Atoms or molecules are liberated from the source and move through the vacuum, with little scattering and low energies, until they deposit onto a substrate. The various evaporation systems in use differ primarily by their evaporation sources and include resistance heating, electron beam heating, cathodic arc, and laser heating. The PVD technique used in the present study employed a cathodic arc evaporation source.
Arc evaporation sources, which operate at low voltages and high currents, create a highly ionized plasma which allows for deposition of adherent coatings at temperatures as low as 200 °C. In this line-of-sight process, components to be coated are placed in a vacuum chamber (Fig 1-5). Following evacuation, an arc is struck on multiple cathodes positioned inside, which, in conjunction with part rotation provide good coating uniformity. The arc flash evaporates and ionizes the source material which is attracted to the negatively biased components. The introduction of a working gas at a small partial pressure allows for the deposition of compounds such as TiN. The main disadvantage of cathodic arc sources is the emission of macroparticles during source evaporation. These unreacted metallic droplets are deposited onto the film’s surface lead to an increase in surface roughness but apparently have little effect on the coating’s tribological properties.  

![Diagram](image)

Figure 1-5. PVD cathodic arc evaporation system. (41)

Nucleation of an evaporated film begins when evaporated atoms strike the substrate surface and become adatoms. These adatoms quickly equilibrate energetically with the surface atoms and diffuse over the surface until they desorb, are trapped energetically at surface adsorption sites (defects such as vacancies or ledges), or join an existing coating nucleus. Growth of PVD films has been observed to occur by three different processes as shown in figure 1-6. The first process, called Volmer-Weber growth, involves nucleation
of distinct and separate three dimensional clusters which, over time, grow into larger clusters or islands. \(^47\) This growth process occurs when the binding energy between coating atoms is greater than the binding energy between the coating atom and the substrate. Only clusters larger than a critical size are stable and can grow. Frank-van der Merwe growth, or two dimensional growth, is the next process and it occurs when coating atoms bind more strongly to the substrate than to each other. \(^47\) In this growth model, adatom surface mobility is high and layer by layer formation of the coating occurs in the absence of a nucleation barrier. Finally, the third growth model, called Stranski-Krastanov growth, is a combination of both island and 2-D growth modes. \(^47\) In this process, the film begins with layer by layer growth until several layers have formed epitaxially, then growth continues by nucleation of discrete islands. The reasons for this transition are not fully understood; however, lattice mismatch between the film and the substrate is thought to play a role.

The microstructure of an evaporated film is influenced primarily by substrate temperature, which influences adatom surface diffusion and bulk diffusion, and surface roughness, which shadows regions of the substrate from the line-of-sight evaporated atoms. Increased temperatures produce smoother, denser, and defect free coatings as a result of the increased surface and bulk diffusion rates. A zone model relating substrate temperature/melting point ratios and gas pressures to film microstructures was devised by the combined efforts of Movchan and Demchishin \(^52\), and Thornton \(^53\) and can be seen in figure 1-7. These researchers discovered that \(T/T_{mp}\) ratios and gas pressures roughly defined distinct microstructures ranging from isolated, columnar crystallites in a low density film, to large, equiaxed grains in a fully dense film.
Zone 1 microstructures, formed at low temperatures (T/T_{np} < 0.15), are porous and consist of tapered crystallites with domed tops separated by voids. This open, columnar microstructure is the result of low adatom surface diffusion which cannot compensate for shadowing of the intercrystallite valleys by the crystallite peaks. These micron sized crystallite columns evolve from a very thin coating/substrate region and are often polycrystalline with small equiaxed grains.

The work by Thorton identified a zone T microstructure which is formed at temperature ratios between 0.15 and 0.45. Surface diffusion is relatively rapid at these temperatures and as a result, these films are more dense and smoother than those previously described. Still, these films contain fibrous grains with high defect densities, mainly dislocations and point defects.

When the substrate/melting point ratios are in the 0.45-0.75 range, adatom surface diffusion is very rapid and dense, coarse columnar microstructures are formed. These larger columns form because of an increase in the bulk diffusion rate and the intercolumn regions are essentially the grain boundaries.

The final microstructural zone identified (zone 3) occurs when the T/T_{np} ratio is above 0.75 and film growth is dominated by bulk diffusion. These microstructures may consist of large, equiaxed or columnar grains which have low defect densities typical of well annealed bulk materials. At these high temperatures, stress and strain free grains form.
readily by recrystallization and, therefore, the resulting coating has low internal residual stresses.

As an alternative to increasing the substrate temperature, zone 1 microstructures can be avoided by bombarding the film with particles during deposition; this process is known as ion plating and will be discussed in a following section. These particles fill the voids between growing crystallites, resulting in a denser film of the zone T type. In PVD processes, bombardment can be provided by the application of a suitable bias to the substrate. As previously mentioned, microstructure has a significant effect on critical film properties such as internal stress, hardness, and adhesion (quantified as critical load from scratch tests). Figure 1-8 shows the variation of these properties as a function of substrate bias voltage for sputtered TiN coatings deposited on stainless steel substrates as reported by S.J Bull. 42

From figure 1-8, it can be seen that the open, columnar microstructure of zone 1 provides good adhesion (critical load) and low internal stresses but possesses a low hardness. As the substrate bias is increased, dense, zone T microstructures, with a hardness comparable to that of bulk TiN, develop. A result of this increased density is an increase in internal stresses and, consequently, a lower critical load capacity. The maximum film thickness which can be deposited is limited by the presence of internal stresses since, at a particular thickness, it becomes favourable for the coating to minimize the stored elastic energy by spallation.

![Figure 1-8. Variation of coating properties: hardness, internal stress, and adhesion (critical load) with substrate bias voltage. (42)
PVD sputter-deposition processes have been in use for over 30 years and are widely used because of their simplicity and because they often offer capabilities superior to that of evaporation. Contrary to evaporation, sputtering is a mechanical process in which highly energetic ions or neutral atoms, accelerated from a plasma or an ion gun, strike the surface of a solid source causing ejection of one or more atoms or molecules by momentum transfer. These sputtered atoms or molecules then travel in a line-of-sight path until they condense on the substrate surface. One of the main advantages of this technique is that the sputtering process removes each solid surface atomic layer consecutively and, if there is no diffusion, the composition of the vapour flux leaving the surface is the same as the bulk of the material being sputtered. This allows for the sputter-vaporization of alloy compositions, something that can not be accomplished with thermally evaporated sources.\textsuperscript{43}

Ion plating, which was briefly mentioned earlier, was developed in the early 1960's and can be used to deposit highly adherent metal, alloy, or ceramic coatings onto virtually any substrate at low temperatures. Essentially a plasma assisted PVD process, ion plating incorporates low energy ion and neutral atom bombardment prior to and during coating growth. Sputtering of the substrate surface prior to coating allows for the removal of surface contaminants (oxides, hydrocarbons) and the production of active nucleation sites (defects). Bombardment during deposition leads to the formation of compounds, such as TiN, excellent adhesion, and the production of dense, equiaxed-grain coatings at low temperatures. In ion plating, the source material to be deposited can be evaporated, sputtered, arc eroded, or formed by some other vaporization method. The main advantage of this technique is its ability to deposit high density, stoichiometric films of compounds such as TiN and ZrN on a wide variety of substrates.

The properties of any thin film are influenced by its microstructure which can be controlled, to an extent, by the processing parameters. However, it must be remembered that there is no simple method for producing a coating which possesses all of the desired properties. Many of these properties are interrelated and are a complex function of the film microstructure, the substrate material, the specimen geometry, and the physics of the deposition process. Usually, there is a trade-off between important properties and these have to be optimized for a specific application.

\textbf{1.3.2 Surface Modification and Fretting}

Few researchers\textsuperscript{34-36} have investigated the effects of surface modification on the fretting corrosion resistance of orthopaedic alloys. The most popular surface modification
techniques employed by those who have, included ion nitriding and nitrogen ion implantation. In fact, only one study included any other process; physical vapour deposition nitriding.

Interested in micromovement at the bone/stem interface, researchers Rabbe et al \(^{15}\) investigated the fretting corrosion resistance of Ti6Al4V and 316L stainless steel against polymethylmethacrylate (PMMA) or ‘bone cement’. These researchers also examined the effect ion nitriding and nitrogen ion implantation had on the fretting resistance of these alloys. Testing was conducted in Ringer’s solution (pH=8) at 25 °C for 100,000 cycles. The normal load between the two planar surfaces was 32 N, the amplitude of slip 80 µm, and the frequency of vibration 1 Hz. Additional testing under the same conditions was performed using a cylindrical PMMA specimen; this produced a maximum Hertzian pressure of 25 MPa. Ion implantation was carried out at both low and high doses, resulting in a solid solution of nitrogen in Ti6Al4V and the precipitation of TiN, respectively. Testing of samples implanted at low doses exhibited good wear resistance, however, the coating was eventually breached and wear proceeded as if the sample was untreated. Conversely, the layer deposited at high doses exhibited excellent wear resistance and no degradation was witnessed. The samples which had been ion nitrided contained a 3 µm thick TiN, TiN\(_2\) layer on a 4 µm thick diffusion layer. Like the samples which had been ion implanted at high doses, the nitrided specimens exhibited no wear or degradation.

Horswill et al \(^{34}\) conducted a study in which they investigated the effects of plasma source ion implantation on the fretting wear behaviour of Ti6Al4V/Ti6Al4V couples. Testing was carried out in dry conditions at a slip amplitude of 200 µm with a frequency of 20 Hz. A flat-on-flat configuration was employed and only one of the surfaces was treated. These researchers reported increased wear resistance for the modified couples and attributed it to the formation of hard, chemically inert, TiN precipitates in the near-surface region of the modified alloy.

Ion implantation, plasma ion nitriding, and physical vapour deposition nitriding were all used by Maurer et al \(^{36}\) to determine whether the fretting corrosion of Ti6Al4V plates and screws (ASTM F-897) could be reduced by treatment of one or both of the surfaces. These tests were conducted in 10% calf serum in a 0.9% saline solution at room temperature for 1.2 million cycles. The magnitude of motion ranged between 0 and 100 µm at a frequency of 1 Hz. The results indicated that treatment of one component, the screws, produced a significant reduction in the amount of weight loss of the untreated plates as well as the screws. Treatment of both components resulted in a further reduction of weight loss.
and plasma nitriding of both surfaces was found to produce the best results. These researchers also observed that once the coating had been removed, the performance of the contact area reverted to that of the untreated couple.

1.3.3 Sol-Gel Thin Films
In addition to the surface modification techniques discussed above, thin ceramic overlay coatings may be deposited through a sol-gel process. The advantages offered by this technique include a non-line-of-sight process, precise microstructural and chemical control, ease of processing, use of relatively low temperatures, development of strong film/substrate adhesion, and minimal equipment costs. In the present study, a polymeric alkoxide-based sol-gel process was used to deposit zirconia ($\text{ZrO}_2$) films onto Ti6Al4V substrates in attempts to investigate the film’s resistance to fretting corrosion. Zirconia is known to be biocompatible and to possess good corrosion and wear resistance; however, no studies investigating the fretting behaviour of these thin films could be found in the literature.

The ‘sol’ is applied to the substrate using spin or dipcoating techniques and is subsequently annealed to produce the desired densification and crystallization. For dipcoating, the withdrawal speed of the substrate and the viscosity of the solution play a significant role in determining film thickness; slower withdrawal rates and lower viscosities result in thicker films. Studies\textsuperscript{44,45} report that, for dip-coating, relatively defect and crack free films can be produced. These films are approximately 100 nm thick and have a crystalline microstructure consisting of metastable cubic and/or tetragonal phases. While an extensive review of the sol-gel process will not be presented here the reader requiring more information should consult the book by CJ Brinker and GW Scherer, Sol-Gel Science: The physics and chemistry of Sol-Gel processing.
2.0 OBJECTIVE

Widely accepted throughout the field of biomaterials, modular implants have developed into complex, multi-alloy devices which, initially, enjoyed a tremendous amount of clinical success. Recently, however, researchers report signs of enhanced degradation and suggest that modular implants possess increased modes of failure when compared to their one-piece counterparts. The mechanism responsible for this accelerated degradation has been identified and several undesirable host responses have been attributed to the metal ions and particulate debris released from modular interfaces. The benefits afforded by modular implants are too important to ignore and a solution which would accommodate these benefits is preferred. Surface modification may represent such a solution as important surface properties can be altered without affecting key bulk properties or implant design. The primary objective of this study was

to determine the effect PVD and sol-gel formed overlay coatings had on the fretting corrosion resistance of titanium/cobalt alloy couples.

Unfortunately, relatively few researchers have investigated the effect commercially available protective coatings have on the fretting corrosion of modular implants, despite the fact that numerous coatings are presently used in the medical industry. Furthermore, little or no information exists on the conditions experienced by these modular connections in vivo; therefore, in vitro testing is limited, somewhat, in its relevancy. The absence of a standard test further complicates the matter as in vitro studies can seldom be compared. As the author chose not to adopt a standardized test intended for osteosynthesis plates and screws, the second objective of this study was

[to design and construct a unique fretting apparatus which was capable of performing multiple tests, simultaneously, in a simulated physiological environment, under conditions of low frequency and small slip amplitudes.]

A coating's resistance to wear and corrosion is related to its thickness, structure, hardness, chemistry, and quality. In efforts to explain the differences between the fretting resistance of the various coatings, the final objective of this study was to

characterize each coating based on its structure, morphology, and chemistry.

This third objective was fulfilled by utilizing common characterization techniques such as electron microscopy, profilometry, and x-ray photoelectron spectroscopy.
3.0 METHODS AND MATERIALS

3.1 MATERIALS

Both the titanium (Ti6Al4V ELI) and cobalt (Haynes-Stellite 25) based alloys used in the present study met the chemical, mechanical, and metallurgical requirements for alloys used in surgical implant applications as specified in ASTM F136 and F90, respectively. The test configuration was such that unmodified Haynes-Stellite 25 spheres were fretted against both modified and unmodified Ti6Al4V flats.

3.1.1 Specimen Preparation

Titanium alloy discs, measuring approximately 4 mm in thickness, were cut from 0.588” diameter bar stock (Dynamet Inc., Washington, PA) using a rotary saw (Isomet Plus precision saw, Buehler, Lake Bluff, IL) and an abrasive cut-off wheel (Buehler No. 11-4217). All discs were mounted in bakelite and one face was ground flat and polished to a mirror finish using an automated polishing unit (AUTOMET® 2 Power Head, Buehler, Lake Bluff, IL). The polishing protocol can be found in appendix A and, in all cases, the final chemomechanical polishing step employed a 0.06 μm colloidal silica suspension (Mastermet, Buehler). After this step, the polished surface was carefully rinsed and wiped as the silica-based solution formed a non-soluble crust upon drying. The Ti6Al4V discs were removed from the bakelite, ultrasonically cleaned in acetone (BDH Inc., Toronto, ON), and dried with forced air.

With the exception of cleaning and passivating (appendix C), no preparation was required for the Haynes-Stellite 25 specimens as they were purchased in spherical form (Industrial Tectonics Inc., Ann Arbor, MI) and used in the as-received condition. The spheres were 0.5” in diameter and had an initial mean surface roughness (Ra) of 0.04 μm.

3.1.2 PVD Surface Modification

In the present study, an industrial supplier, who specializes in coatings for the medical industry (Multi-Arc Inc., Rockaway, NJ), coated the Ti6Al4V discs with titanium nitride (TiN), zirconium nitride (ZrN), and amorphous carbon coatings. Cathodic arc evaporation and enhanced arc evaporation were the processes used to deposit the nitride (TiN and ZrN) and carbon films, respectively. The enhanced evaporation process uses high strength magnetic fields to suppress microparticle emission and increased film/substrate adhesion is an apparent result. Unfortunately, deposition variables such as pressure, time, and temperature were unknown to the author as a result of proprietor confidentiality.
3.1.3 Zirconia Sol Preparation

Deposition of the sol-gel-formed zirconium oxide (zirconia) coating began with the preparation of a zirconia precursor solution. A 70% solution of zirconium propoxide, \(\text{Zr}([\text{OC}_3\text{H}_7])_4\), in n-propanol (Johnson Matthey Ltd., Ward Hill, MA) was the source of the zirconium and acetic acid (BDH Inc., Toronto, ON), acting as a chaleting agent, slowed the hydrolysis of the alkoxide. The addition of double distilled water catalyzed the hydrolysis and condensation reactions required for zirconia polymerization and ethylene glycol (Mallinckrodt AR) was used as a plasticizer to help prevent fracture of the gel film during drying. A complete description of the precursor preparation can be found in appendix B. After the zirconia sol was prepared, it was stored in a sealed container at room temperature and ‘aged’ for several days.

3.1.4 Sol-Gel Dip-coating Process

The present study employed a dip-coating process to deposit the sol-gel derived zirconium oxide film. In this process, film thickness is controlled by both sol viscosity and the rate of specimen withdrawal. Earlier work by Filiaggi identified a relationship between the two for various sol viscosities and indicated that 100 nm thick films were free of defects induced by cracking of the film during the drying stage.

Sol viscosity was measured using a rotary viscometer with a low viscosity adapter (Model LVF, Brookfield, Stroughton, MA) and, from the work of Filiaggi, it was determined that a specimen withdrawal rate of 5 cm/min would be required to produce a 100 nm thick \(\text{ZrO}_2\) film. The dip-coating apparatus (Fig 3-1) used a vertically mounted screw-driven gliding unit (UniSlide, Velmex Inc., East Bloomfield, NY), a PC controlled stepping motor, and customized software to reproducibly control film thickness.

Prior to coating, all Ti6Al4V substrates were ultrasonically cleaned and passivated using the procedure outlined in appendix C. The titanium alloy substrate was clamped to the sliding unit (Fig 3-2) and slowly immersed until the level of the sol approached the end of the clamp. After sitting in the sol for 10 seconds, the specimen was withdrawn at the specified rate until it was completely out of the precursor solution. The dip-coating process was carried out in a class 100 laminar flow hood (h, EdgeGARD model IV-22, Baker, Sandford, Maine) in efforts to reduce surface contamination by airbourne particulates.
Once the coated Ti-alloy substrates appeared visually dry they were carefully removed from the clamp and transferred to a muffle furnace (Thermolyne 48000, Dubuque, Iowa) for annealing. All specimens were annealed for one hour at 500 °C and the heat treatment protocol was as follows: ramp from room temperature to 475 °C at a rate of 5 °C/min.; ramp from 475 °C to 500 °C at a rate of 1 °C/min.; hold at 500 °C for one hour; and furnace cool. The heat treatment was performed in air.
3.2 FILM CHARACTERIZATION

3.2.1 Coating Morphology, Thickness, and Structure

A low-voltage field emission scanning electron microscope (Hitachi S-4500) was used to examine the morphology of the PVD and sol-gel derived coatings. Film defects such as holes, cracks, or particles, were investigated using secondary electrons (SE), accelerating voltages between 10 and 20 KeV, and various magnifications.

Coating thickness was determined by examining the cross-section of modified Ti-alloy discs with the SEM. Only the thickness of the PVD films could be determined in this manner as the sol-gel-formed coating was too thin. Coated substrates were sectioned and polished using the equipment and techniques discussed in section 3.1.1, ultrasonically cleaned in acetone, and examined with secondary electrons using accelerating voltages of 10 and 20 KeV.

The structure of the PVD films was examined by freeze fracturing. Using a rotary saw, modified discs were partially sectioned by cutting the discs from the underside towards the coating. The partially sectioned substrates were then immersed in liquid nitrogen for 2 minutes and fractured. Following fracture, the samples were ultrasonically cleaned in acetone and examined with the SEM (SE detection, 10 KeV).

3.2.2 Sol-Gel Film Thickness

The thickness of the sol-gel derived zirconia film was determined using an automated ellipsometer (AUTO EL*-II, Rudolph Research, Flanders, NJ). The signal wavelength used was 6328 Å and, based on earlier work [48], the refractive index of the film was chosen as 1.90. The thickness values were calculated from the Δ and Ψ parameters and, in all cases, thickness measurements were taken near the centre of the disc where the fretting would subsequently occur and edge effects were non-existent.

3.2.3 Chemical Analysis

The chemistry of the films was characterized using energy dispersive x-ray spectroscopy (Hitachi S-4500 with Links System EDX) and x-ray photoelectron spectroscopy (XPS) techniques. XPS depth profiling was performed with a Leybold MAX 200 system using unmonochromatized Mg or Al Kα x-ray radiation. The Mg x-ray source was operated at 15 KeV and 20 mA while the Al source was operated at 15 KeV and 25 mA. Spectra were collected in low resolution mode with a 192 eV pass energy. The sputtering beam, formed from Ar ions at 5 KeV, had a 1 mm spot size and was rastered over a 2x2 mm area. A complete description of X-ray photoelectron spectroscopy and
depth profiling techniques can be found in the book edited by D Briggs and MP Seah, Practical surface analysis: Vol II - Auger and x-ray photoelectron spectroscopy.

3.3 EXPERIMENTAL APPARATUS

The absence of a standard test for measuring the fretting corrosion of modular implants made it necessary for the author to design and construct a unique fretting apparatus. The device performed multiple tests, simultaneously, in a simulated physiological environment maintained at body temperature (37 °C). A wide variety of specimen geometries and load conditions could be accommodated and tests were conducted at low frequencies and small slip amplitudes for extended periods of time. A complete description of the device will be presented in the following sections, beginning with a discussion on the generation of the fretting movement.

3.3.1 Fretting Device: Movement

The fretting device consisted of three parallel stainless steel bars mounted on a large aluminum plate (Fig 3-3). The two outside bars served as sliding rails and each contained four inverted spring-loaded linear bearings. The center bar was a drive shaft connected to an AC motor with a 5:1 gear ratio; a motor speed of 60 rpm produced a shaft rotation speed of 12 rpm (Fig 3-4).

Figure 3-3. Central drive shaft and two sliding rails with four spring loaded linear bearings.
Positioned on the slide rail, between each pair of spring-loaded bearings, was a push-rod which extended out, perpendicularly, from the slide rail towards the drive shaft (Fig 3-5). There were four push-rods in total, each guided by its own linear bearing. The push-rods were aligned such that two, one from each rail, met the drive shaft at the same point. At that point, an eccentric cam was fastened to the drive shaft and the two push-rods were connected with a metal plate.

As the cam rotated counter-clockwise, through 180°, it pushed the rod, marked A, towards the left rail. Simultaneously, the rod marked B was being pulled away from the opposing rail (not seen). During cam rotation through the next 180°, the effect was reversed and the rod marked A was pulled back to its starting position.
The design of the cams was such that the push-rods oscillated, sinusoidally, at a frequency of 0.2 Hz and an amplitude of 0.5 cm.

At the sliding rail end of each push-rod was a wedge-shaped component containing an elliptical hole through which the rail was able to pass (Fig 3-6). Note the very slight angle of the wedge.

Figure 3-6. Wedge at the end of push-rod.

The wedge of the push-rod was positioned on the slide rail between the two spring-loaded linear bearings (Fig 3-7). Between the bearings and the push-rod were half wedges which were able to slide back and forth on the rail. The half wedges were machined at the same angle as the push-rod wedge so that the angled surfaces of these three components met flat. The 0.52° angle of the wedges (Fig 3-6) was such that a forward push-rod movement of 0.5 cm (from cam rotation) produced a 50 μm lateral movement of the spring-loaded bearings. This was how the first half of the fretting cycle was generated.

Figure 3-7. Push-rod/wedge/spring system. Responsible for fretting motion of linear bearings.
The return half of the fretting cycle was produced by the springs mounted on the slide rail. As the cam pulled the push-rod back, the springs returned the bearing to its original position. This was an important aspect of the design, however, as the springs had to be carefully chosen. To move the bearing, the push-rod had to overcome the opposing force of the spring, which increased as the bearing moved farther along the rail. A high coefficient of friction could arise between the two fretting samples and, depending on the normal load, a large frictional force would develop. During the return half of the fretting cycle, the spring had to overcome this frictional force and return the bearing to its original position.

Using a spring with a large spring constant would ensure that the frictional forces were overcome during the return cycle. However, too stiff a spring would prevent the push-rod from moving the bearing the entire fretting distance. Conversely, a spring with a small spring constant would permit movement of the bearings by the push-rod, but might not have been strong enough to overcome the frictional forces and complete the entire fretting cycle. Furthermore, the springs had to be pre-loaded to overcome the frictional force, which was constant provided that \( \mu \) was constant, as the bearing returned to its original position and the spring displacement approached zero.

### 3.3.2 Fretting Device: Components

The titanium alloy discs and cobalt alloy spheres were secured into cylindrical acrylic specimen holders which were 1.5" in diameter and had a height of 13 mm and 16 mm, respectively. The Ti holder had a 0.6" diameter hole recessed into its center such that the Ti-alloy disc protruded between 1 and 2 mm above the surface of the holder (Fig 3-8a). Similarly, the cobalt-alloy sphere holder had a 0.55" diameter hole recessed into its center; the sphere protruded between 3 and 4 mm above the surface of the holder (Fig 3-8b). Both specimens were secured into their holders with epoxy.

![Figure 3-8. (A) Titanium alloy disc acrylic specimen holder. (B) Cobalt alloy sphere acrylic specimen holder.](image-url)
Mounted onto the spring loaded bearings were round ‘bearing blocks’ which had a recessed hole in the center and used three steel screws (120° apart) to secure the Ti-alloy specimen holders into place (Fig 3-9a and 3-9b).

![Bearing block on top of spring loaded linear bearing.](image1)

(A)

![TiN sample in specimen holder secured into bearing block.](image2)

(B)

Figure 3-9. (A) Bearing block on top of spring loaded linear bearing. (B) TiN sample in specimen holder secured into bearing block.

Once the specimen holder was secured, a test container made entirely out of plexiglass, in order to avoid any galvanic corrosion effects, was placed on top of the ‘bearing block’ (Fig 3-10). The hole in the bottom of the test container aligned perfectly with the specimen holder and the test container was made water-tight by sealing with silicone caulking.

![All-plexiglass test container](image3)

Figure 3-10. All-plexiglass test container

37
A plexiglass lid, containing a large square hole through which the 'loading arm' passed, fitted snugly onto the test container (Fig 3-10). The lid had three other holes; the center one was used for taking temperature and pH measurements while the other two allowed plastic tubing to enter and exit the test container. Acting like a heat exchanger, these tubes circulated hot water and maintained the test solution at a specified temperature.

Two elevated stainless steel bars, running directly above the push-rods, contained four 'load arms' each (Fig 3-11a). These 'arms' were designed such that two could be mounted onto the bar at the same place and face in opposite directions. Like the bearing blocks, these components had a recessed hole in the center and used three steel screws to secure the Co-alloy sphere specimen holders into place (Fig 3-11b).

![Figure 3-11](image)

(A) Four 'loading arms' containing Haynes-Stellite 25 spheres. (B) Alignment of sphere relative to Ti disc. Arms are able to swing on bar.

The 'load arms' were able to swing on the elevated stainless steel bars allowing easier specimen accessibility (Fig 3-11b). Unfortunately, the machining tolerances of the holes, through which the support bars passed, permitted some movement of the arms in the fretting direction. Therefore, the relative movement between the Co-alloy spheres and the Ti-alloy discs was equal to the movement of the 'bearing blocks' minus the movement of the 'arms'. Movement of both components was measured with a precision dial meter which was calibrated with an Instron 8501 servohydraulic mechanical testing machine.
3.3.3 Sample Preparation and Test Set-Up

Prior to testing, all samples were ultrasonically cleaned and passivated as outlined in appendix C. Each sample was then epoxied (LePage 11 regular epoxy) into its respective specimen holder and left overnight while the epoxy hardened. After the epoxy had cured, the Ti-alloy specimen holders were secured into their respective 'bearing blocks' with three steel screws. Plexiglass test containers were placed on top of the bearing blocks and sealed in place with silicone caulking (All-purpose Silicone Seal). The silicone was allowed to cure overnight.

A small (10 cm x 10 cm) sheet of latex was placed between the 'loading arm' and the cobalt alloy specimen holder. This sheet of latex was wrapped around the outside of the loading arm after the specimen holder was secured into place and prevented the metallic arm from coming into contact with the test solution; eliminating any galvanic corrosion effects which would have otherwise occurred. The edges of the latex sheet were fastened to the plexiglass lid, on the top surface around the large square hole, using double-sided tape.

Prior to testing, Tygon tubing (3/16" OD x 1/16" ID) was inserted through one of the holes of the lid, looped around the cobalt alloy specimen holder, and brought back out through the other hole. These tubes were attached to an immersible circulator (Lauda, type B) which circulated hot water and maintained the test solution at a specified temperature. To keep the test solution at 37 °C, it was determined that the temperature of the water circulated through the tubes had to be between 48 and 50 °C. The immersible circulator ensured that the water temperature was maintained throughout the duration of the test.

The containers were filled with 30 ml of buffered Hank's solution. The solution was prepared by mixing salts in powder form with low-resistivity distilled water and buffering to a pH of 7.3 ± 0.2 with HCl and NaOH. The constituents of Hank's solution are listed in table 3-1 and the preparation protocol described in appendix D.

<table>
<thead>
<tr>
<th>Table 3-1. Hank's Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams/Litre</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>CaCl₂•2H₂O</td>
</tr>
<tr>
<td>MgSO₄•7H₂O</td>
</tr>
<tr>
<td>NaHCO₃</td>
</tr>
</tbody>
</table>
After the container was filled with Hank’s solution, the two specimens were brought into contact by carefully lowering the loading arm down until the Co-alloy sphere came into contact with the Ti-alloy disc. The lids were gently placed on the test containers and the test was started.

3.3.4 Test Conditions

The weight of the load arms and the diameter of the cobalt spheres was such that the maximum contact stress between the two specimens was equivalent to approximately 600 MPa (see appendix E). The AC motor operated at a speed of 60 rpm and, with the 5:1 gear ratio between the motor and the drive shaft, produced a frequency of oscillation equal to 0.2 Hz. As mentioned previously, the 0.5 cm oscillation of the push-rods produced a 50 μm movement of the linear bearings. The manufacturing tolerances of the load arms permitted some movement in the fretting direction and, as a result, the relative slip amplitude between the spheres and discs was approximately 26 μm. All tests were conducted in Hank’s solution at 37 °C for 14 days. This produced approximately 240,000 fretting cycles.

Twenty four titanium alloy discs were used in three fretting tests; eight specimens per test. The distribution of the materials is shown in table 3-2. As the fretting contact area was very small, only eight cobalt alloy spheres were required and each was used three times. The fretting damage on each sphere was labeled and care was taken to ensure that each test used an undamaged section of the Co-alloy surface.

Table 3-2. Distribution of test materials

<table>
<thead>
<tr>
<th>Material</th>
<th># of specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V</td>
<td>6</td>
</tr>
<tr>
<td>TiN</td>
<td>6</td>
</tr>
<tr>
<td>ZrN</td>
<td>3</td>
</tr>
<tr>
<td>AC</td>
<td>6</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>3</td>
</tr>
</tbody>
</table>

3.3.5 Single Pass Test

In addition to the test described above, a single pass test was performed. In this case, the specimens were prepared, mounted, and secured into the fretting device as previously discussed. Instead of using the immersible circulator and heat-exchanger tubes, however, the buffered Hank’s solution was heated to 37 °C using a hot-plate. The containers were filled with this heated solution, the cobalt alloy spheres were gently lowered onto the titanium alloy discs, and one full rotation of the drive shaft was performed.
by hand. This resulted in one fretting cycle. The specimens were removed from their containers, ultrasonically cleaned, and examined under the SEM as described below.

3.4 FRETTING WEAR ASSESSMENT

After testing, all samples were removed from their specimen holders and treated in EDTA in efforts to remove any calcium phosphate deposits which may have precipitated from the Hank's solution during testing. Subsequently, all samples were ultrasonically cleaned using the cleaning and degreasing protocol found in appendix C but the samples were not re-passivated. The resultant surface damage on both the titanium and cobalt alloy specimens was assessed using scanning electron microscopy and non-contact optical profilometry.

3.4.1 Scanning Electron Microscopy

The fretted surfaces were examined with a low-voltage field emission scanning electron microscope (Hitachi S-4500) using secondary electron detection. Accelerating voltages varied between 10 and 20 KeV and all Ti-alloy discs samples were viewed at a tilt angle of 55° with the axis of rotation parallel to the fretting direction.

3.4.2 Non-Contact Optical Profilometry

Surface roughness and wear scar dimensional analysis was examined with a Wyko NT2000 profilometer. This instrument uses the principal of white light interference to obtain surface information on the nanometer scale. The device was operated in the VSI (vertical scanning interferometric) mode at magnifications of 5.3x and 10.2x. The tilt correction function was used to alleviate the problem of specimen alignment.
4.0 RESULTS AND DISCUSSION - Material Characterization

4.1 SURFACE MORPHOLOGY

4.1.1 Roughness

The roughness of each surface was evaluated using a non-contact optical profilometer and the results are presented in table 4-1. The average surface roughness parameter, Ra, was chosen as a means to characterize the test surfaces prior to fretting and to obtain specific information about the roughness of each coating. The average roughness parameter represents the area between the roughness profile and its mean line and is defined by \( Ra = \frac{1}{L} \int |r(x)| \, dx \), where \( L \) is the length of the profile and \( r(x) \) is the height (or depth) of the profile relative to the mean line. All specimens were prepared in the same manner and, therefore, prior to coating, all started with the same roughness as the unmodified Ti6Al4V discs; 0.027 \( \mu \text{m} \).

Table 4-1. Initial Surface Roughness Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra (( \mu \text{m} ))</th>
<th>Sample</th>
<th>Ra (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti6Al4V</td>
<td>0.027</td>
<td>Carbon</td>
<td>0.051</td>
</tr>
<tr>
<td>TiN</td>
<td>0.046</td>
<td>Zirconia</td>
<td>0.025</td>
</tr>
<tr>
<td>ZrN</td>
<td>0.045</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The two PVD nitride films (TiN and ZrN), applied with a cathodic arc evaporation process, were significantly rougher than the underlying substrate. Roughness values of 0.046 \( \mu \text{m} \) and 0.045 \( \mu \text{m} \) were exhibited by the TiN and ZrN coatings, respectively. This increased roughness was attributed to the emission of macroparticles and the development of pinholes during film growth.

The amorphous carbon film was deposited using an enhanced arc evaporation process which used high strength magnetic fields to suppress macroparticle emission. Consequently, these films were expected to have Ra values much lower than the TiN and ZrN films deposited using the standard process; however, from table 4-1, it can be seen that the carbon coating possessed the greatest surface roughness. Unlike the nitride films, this increased roughness was attributed to a surface texture which can been seen in figure 4-1. While these carbon coatings were virtually free of macroparticles, they did contain surface pits or holes which may have also contributed to the increased roughness (see Fig 5-22).
The sol-gel-formed zirconium oxide coating had a surface roughness equivalent to that of the Ti-alloy substrate. This was a direct result of the dip-coating process and the ZrO₂ nanometre scale film thickness.

![Image](10.0kV x60.1K  500nm)

**Figure 4-1.** High magnification image of amorphous carbon film surface.

### 4.1.2 Film Defects

Examples of various defects associated with thin overlay films can be found in figures 4-2 to 4-9. As previously mentioned, common defects associated with PVD films include macroparticles and pinholes. Macroparticles are unreacted metallic droplets ejected from the source during evaporation. These particles accelerate towards the substrate at high speeds and embed themselves into the surface of the film. While they, reportedly ⁴⁷, have little effect on the coating’s tribological properties, it seems reasonable to suggest that, if ejected from the film, these particles could have a serious effect on the coating’s performance. Particles removed from the coating’s surface could act as third-body abrasives and accelerate the wear of the coating and/or the counter surface. Examples of macroparticles can be seen in figures 4-2 and 4-6.

Pinholes are unavoidable and are the result of the film growth mechanism discussed in section 1.3.1. A pinhole which protrudes through the film, exposing the substrate, may compromise the corrosion resistance of the coating and, therefore, minimizing these defects
is important. An excellent example of a pinhole can be seen in figure 4-3. Figures 4-4, 4-5, and 4-7 exhibit larger defects often associated with PVD films; defects which can be very large (Fig 4-4) and/or protrude directly through the film (Fig 4-7). However, it is believed that the majority of these large defects do not protrude through the entire film and figure 4-5 shows an example of this.

Although macroparticles are absent in sol-gel-formed films, defects, in the form of cracks and pinholes, do exist, however, particularly in areas of increasing film thickness. Examples of sol-gel film defects can be found in figures 4-8 and 4-9. Small diamond-shaped cracks, resulting from contaminants present on the substrate surface prior to coating, can occur anywhere on the sol gel film surface. In the present study, the quality of the sol-gel-formed zirconia films was quite good as only a few cracks could be found (Fig 4-8) and no pinholes were observed.

Near the edges of the ZrO₂-coated discs, where the film thickness was greatest, long, interconnected cracks were observed (Fig 4-9). These cracks were the result of large internal stresses which developed with increasing film thickness. In the present study, fretting occurred at the centre of the sol-gel-coated discs and the presence of these 'edge' cracks was not a concern.

Figure 4-2. Macroparticle embedded into TiN film.
Figure 4-3. Pinhole and hole left by ejected particle in TiN film.

Figure 4-4. Large defect in TiN film.
Figure 4-5. Hole in TiN film. Substrate not exposed.

Figure 4-6. Cracked macroparticle embedded into ZrN film surface.
Figure 4-7. Defect in ZrN film. Substrate may be exposed.

Figure 4-8. Crack in sol-gel-formed zirconium oxide coating.
4.2 FILM THICKNESS

4.2.1 Physical Vapour Deposition Films (TiN, ZrN, AC)

The thickness of each PVD film was determined by sectioning a coated disc and polishing the sectioned surface to a mirror finish using the protocol found in appendix A. The cross-sectioned films were then examined with the SEM and the thickness of each film was determined from the micrographs found in figures 4-10 through 4-12.

Figure 4-10 represents the polished edge of a sectioned TiN coated disc and, from this micrograph, it can be seen that the coating was uniform with a thickness equal to 3 μm. The film/substrate interface was planar and consistent and some macroparticles could be seen embedded into the coating’s surface.

A micrograph of the sectioned zirconium nitride coating can be seen in figure 4-11. As with the TiN sample, the thickness of the ZrN film was approximately 3 μm. The ZrN coating exhibited a uniform thickness but, unlike the TiN film, small dark spots could be seen throughout the edge of the film. While some of these large spots were thought to be contaminants, it was believed that a few, marked by the arrows, were small pits or pores left in the film’s edge from the abrasive action of polishing.
Figure 4-10. Polished cross-section of a TiN coated disc.

Figure 4-11. Polished edge of ZrN cross-section.
A cross section of the amorphous carbon coating can be seen in figure 4-12 and, unexpectedly, two distinct layers were present. Although these two layers differed in appearance, each was uniform with a thickness equivalent to 2 μm. It was assumed that the upper layer was the carbon film and that the bottom layer was present in an attempt to improve the adhesion of the AC layer to the substrate. X-ray studies, discussed in a following section, were performed in order to identify the composition of these layers. It should be noted that, unlike the TiN and ZrN films, large sections of the AC coating were removed from the substrate during polishing (Fig 4-13). As all sectioned specimens were prepared in the same manner, this result suggested poor AC film/substrate adhesion compared to that of the nitride films.

4.2.2 Sol-Gel-Formed Zirconia

As the thickness of the sol gel formed coating was in the 100 nm range, film thickness was determined using automated ellipsometry. All measurements were taken at the centre of the coated discs where the fretting experiments would subsequently occur. The average ZrO₂ film thickness, measured from several specimens prepared with the same sol under the same coating conditions, was equal to 100 nm.
4.3 FILM MICROSTRUCTURE

4.3.1 Amorphous Carbon

Representative fractured surfaces of the multi-layered carbon film, produced by polishing and freeze fracturing, can be seen in figures 4-13 and 4-14, respectively. Both micrographs revealed distinct structural differences between the two layers. The bottom layer had a very pronounced columnar structure and appeared dense; whereas, the upper, darker layer had a very irregular structure. The marked contrast in structure further suggested a compositional difference between the two layers.

The surface texture of the carbon film could clearly be seen in figure 4-14; as could two surface features, marked by the white arrows, which resembled macroparticles. The striations seen in the fractured amorphous layer, marked by the black arrow, appeared to show some ordered structure but, as no structure could be found in figure 4-13, it was believed that these striations were formed upon fracture. Further evidence of this will be presented when discussing the structure of the ZrN film.

![Figure 4-13. Fractured edge of carbon film. Piece of the edge broke off during polishing. Note difference in structure between the two layers.](image-url)
Figure 4-14. Fractured amorphous carbon film produced by freeze fracturing.

Figure 4-15. Fractured surface of TiN coating.
4.3.2 *Titanium Nitride (TiN)*

Analogous to the bottom layer of the carbon film, the microstructure of the titanium nitride coating appeared dense with a columnar structure (Fig. 4-15). The TiN columnar structure was less pronounced, however, suggesting an increased coating density compared to that observed with the carbon film. The structure of the TiN film was typical of a zone T microstructure which produces smooth and dense films containing fibrous grains. While these zone T microstructure films have a high hardness, their dense structure results in large internal stresses which limits coating thickness and reduces the film's critical load capacity. This microstructure was representative of the TiN coatings.

4.3.3 *Zirconium Nitride (ZrN)*

The structure of the ZrN coating (Fig 4-16 and 4-17) was very similar to that of the TiN film; dense with a columnar structure typical of a zone T microstructure. The ZrN film appeared extremely dense and may have contained very high internal stresses as small cracks, marked by the black arrows, could be seen at certain points throughout the film (Fig 4-16 and 4-17). It should be noted that no cracks were observed in any of the other coatings.

During fracturing, it was believed that a thin layer of the ZrN coating remained adhered to the substrate while the majority of the coating broke away (Fig 4-16). The presence of a circular defect at the bottom of the micrograph (Fig 4-16), marked by the white arrow, was the foundation of this theory. Similar defects had been found on the surface of the fractured carbon film and the presence of such a defect on the Ti6Al4V substrate was thought to be unlikely. Evidence supporting this theory can be found in figure 4-17, where it can be seen that a thin layer existed between the substrate and the bulk of the film. While this layer may have been an intermediate coating used to improve film/substrate adhesion, it was most likely part of the ZrO₂ coating which remained adhered to the substrate while the rest of the film broke away.

Close examination of the circular defect in figure 4-16 revealed that it had the same striations as those found in the fractured amorphous carbon layer (Fig 4-14). The appearance of these striations in both the ZrN and carbon films reinforced the hypothesis that these marks occurred from fracture and were not representative of the ordered structure of the AC film. Also of interest in figure 4-16 was a macroparticle embedded into the ZrN film and the cross-section of a hole which was formed by such a particle.
Figure 4-16. Fractured surface of ZrN film.

Figure 4-17. ZrN fractured surface showing possible intermediate layer.
4.4 CHEMICAL COMPOSITION

4.4.1 X-Ray Microanalysis

Chemical composition was characterized using energy dispersive x-ray spectrometry and the spectra for each material can be found on the following pages. It should be noted that the peak at 0 keV is a reference peak used by the EDX system for calibration. Figure 4-18 is the EDX spectrum of the unmodified titanium alloy and strong peaks corresponding to the major constituents (Ti, Al, and V) were observed.

The incident x-rays had insufficient energy to pass through the thick TiN film and excite the atoms of the substrate; consequently, a peak associated with nitrogen emerged while the Al peak disappeared (Fig 4-19). The titanium peak at approximately 0.43 KeV had an increased intensity, as compared with the Ti6Al4V spectrum, and slightly overlapped the nitrogen peak.

EDX analysis of the ZrN surface (Fig 4-20) produced an interesting result. While a strong zirconium peak was present, the intensity of the nitrogen peak was very weak; suggesting a coating comprised almost entirely of Zr. This peculiar result could not be explained through further EDX studies and, therefore, XPS studies were conducted. These results will be discussed in a following section.

The EDX spectrum for the carbon coating can be seen in figure 4-21. Associated with the large carbon peak were smaller peaks indicating traces of titanium, nitrogen, and oxygen. The presence of Ti and N was puzzling as this film was observed to be 4 μm thick and excitation of the substrate was unlikely. As with the ZrN film, XPS studies were conducted in efforts to explain these results.

The EDX spectrum for the surface of the sol gel formed zirconia film can be found in figure 4-22. As expected, peaks corresponding to zirconium, oxygen, titanium, aluminum, and vanadium were observed. The presence of the three substrate elements (Ti, Al, and V) was expected as the ZrO₂ film was too thin to prevent interaction between the incident x-rays and the substrate.
Figure 4-18. EDX spectrum of unmodified Ti6Al4V surface.

Figure 4-19. Surface spectrum for TiN coating.
Figure 4-20. EDX spectrum of ZrN surface. Note small N peak.

Figure 4-21. Spectrum for amorphous carbon surface. Peaks for Ti, N, and O are observed. Unidentified peak exists at approximately 2 keV.
4.4.2 **EDX Linescans**

Linescan measurements were taken across the polished edge of each PVD film in an attempt to obtain information on compositional changes occurring throughout the thickness of the film. Some unexpected results were obtained and the linescans for each film can be found in figures 4-23 through 4-25. Unfortunately, this information was qualitative and the relative intensity of the lines could not be compared to each other.

Figure 4-23a is an electron micrograph of the sectioned TiN coating used for the linescan studies and the white line drawn across the film represents the EDX scanning path. The elements examined included titanium, nitrogen, and aluminum and the change in the relative intensity of each element throughout the thickness of the film can be seen in figure 4-23b. It can be seen that the nitrogen level remained high throughout the bulk of the film and slowly decreased towards the film/substrate interface. This result was expected given the low content of N in the Ti6Al4V alloy (0.05 wt % Max.). Unexpectedly, both the Ti and Al levels remained low approximately 1.5 μm into the substrate. This result was thought to be an artifact caused by a geometrical effect. The peak in the SE line around 4.5 μm (Fig 4-23b) indicated a change in specimen geometry and it was believed that a 'step' existed at the film/substrate interface. As TiN is much harder than Ti6Al4V, it was believed that the film was higher than the substrate and that the x-rays emerging from the Ti alloy, just below the film/substrate interface, had to pass through the TiN film before being
detected. Many of these substrate x-rays would be absorbed by the film during this process and this may account for the low levels of Ti and Al in this region.

The EDX linescan across the ZrN film can be seen in figure 4-24b and the elements examined included nitrogen, titanium, aluminum, and zirconium. A clear distinction between the film and the substrate was observed at approximately 3.7 μm, where the zirconium level sharply dropped and the Ti level suddenly rose. Unlike the TiN film, the intensity of the N line remained uniform throughout the scan; suggesting that the N content in the ZrN film was no higher than it was in the Ti alloy substrate. Although inexplicable, this result was consistent with the EDX surface scans which exhibited a very weak N signal. Nitrogen has a low atomic number and it was suggested that the nitrogen x-rays were being absorbed by the detector window of the EDX system. However, all specimens were examined under identical EDX conditions and nitrogen was detected in both the TiN and AC films. XPS studies were performed in efforts to explain these results.

The linescan for the carbon film (Fig. 4-25b) verified the hypothesis, made in section 4.2.1, that the upper, amorphous layer was carbon. From this figure, it could be seen that the carbon level started to decrease near the multi-layer interface and was completely absent midway through the columnar layer. The titanium, aluminum, and nitrogen levels were low throughout the first layer and, while the Al level remained low throughout the entire film, a rise, and subsequent fall, in both the Ti and N levels was experienced throughout the intermediate layer. This result suggested that the intermediate layer was TiN, used to improve the adhesion of the carbon film to the substrate. XPS studies, discussed in the following section, were conducted in efforts to verify these results and identify the elemental composition of the intermediate layer. The presence of a TiN layer would help to explain why titanium and nitrogen peaks were observed in the carbon EDX spectrum (Fig 4-21) as the amorphous carbon layer may not have been thick enough to prevent excitation of the underlying columnar layer.
Figure 4-23a. Micrograph of TiN film used for linescan.

Figure 4-23b. Elemental linescan across TiN film.
Figure 4-24a. Micrograph of ZrN film used for linescan.

Figure 4-24b. Elemental linescan across ZrN film.
Figure 4-25a. Micrograph of AC film used for linescan.

Figure 4-25b. Elemental linescan across AC film.
4.4.3 XPS Studies

XPS depth profiling was used to further examine the three PVD films and to help explain some of the peculiar results discussed in the previous section. The films were sputtered with Ar ions for 45 minutes then sampled with Al and/or Mg x-rays, repeatedly, until the film was breached. In most cases, depth profiling continued well into the substrate.

Figure 4-26 is a plot of the relative atomic % of several elements in the ZrN film versus the depth into the specimen. The elements examined included oxygen, titanium, nitrogen, carbon, and zirconium. Table 4-2 represents the relative atomic % of each element at certain points within the film and a depth of 0.0 \( \mu \text{m} \) represents an initial surface scan prior to sputtering.

Figure 4-26. Relative atomic % vs. Depth into the ZrN film for O, Ti, N, C, and Zr.

<table>
<thead>
<tr>
<th>Depth (( \mu \text{m} ))</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
<th>C</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>36.23</td>
<td>0.0</td>
<td>9.68</td>
<td>29.33</td>
<td>24.76</td>
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<td>43.18</td>
<td>0.0</td>
<td>53.99</td>
</tr>
<tr>
<td>2.9</td>
<td>2.06</td>
<td>7.18</td>
<td>39.92</td>
<td>0.0</td>
<td>50.84</td>
</tr>
<tr>
<td>3.2</td>
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<td>60.69</td>
<td>28.05</td>
<td>0.0</td>
<td>8.77</td>
</tr>
<tr>
<td>3.8</td>
<td>6.20</td>
<td>65.88</td>
<td>22.40</td>
<td>0.0</td>
<td>5.52</td>
</tr>
<tr>
<td>5.1</td>
<td>6.62</td>
<td>63.01</td>
<td>28.87</td>
<td>0.0</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Table 4-2. Relative atomic % of elements in ZrN film.
The large relative amount of carbon and oxygen recorded during the initial scan was due to surface contamination and the presence of a zirconium oxide layer. This was evident by the fact that the O and C levels dropped off immediately after sputtering began. While the zirconium and nitrogen levels remained constant between 0.33 μm and 2.64 μm, the Ti, C, and O levels were near zero. These scans represented the bulk of the ZrN film and, contrary to the EDX results, indicated that the relative amount of nitrogen in the ZrN film was quite high. A sharp drop in the Zr and N levels, and a corresponding increase in the Ti content, at a depth of approximately 2.97 μm indicated that the film/substrate interface had been passed and verified that the thickness of the ZrN coating was roughly 3.0 μm.

In contrast to the EDX line scans, the N level was reduced at the film/substrate interface and remained very high for at least 3 μm into the titanium alloy. As previously mentioned, the maximum composition of N in Ti6Al4V is 0.05 wt % and conversion into atomic percent gives a Ti:N ratio of approximately 524. Using the data (depth = 3.8 μm) from table 4-2, it was determined that the ratio of Ti to N, 0.8 μm below the film/substrate interface, was equal to 2.94. This finding suggested abundant diffusion of N into the substrate during the coating process. While this result did not explain the absence of N in the ZrN EDX scan (Fig 4-20), it may have explained why the ZrN line scan (Fig 4-24b) maintained a uniform N level across the film/substrate interface as the change in the relative atomic % of N, from 44 to 25 (Fig 4-26), may have been too small for the EDX system to detect.

The XPS data for the TiN film can be seen in figure 4-27 and the relative amount of each element at various depths in the film can be found in table 4-3. As with the ZrN film, the surface of the TiN film was covered with contaminants and thin oxide films which resulted in large relative amounts of O and C during the initial surface scan. Sputtering quickly removed these films and, at a depth of 0.4 μm, the bulk of the TiN film was being sampled.

Large changes in the nitrogen and titanium levels began approximately 2.4 μm into the film and were complete by a depth of 3.5 μm, indicating that the film/substrate interface had been passed and that the TiN coating was approximately 3.0 μm thick. This gradual reduction in the N level was the result of both nitrogen diffusion into the substrate and the sputtering process. A ‘knock on’ effect, in which sputtered atoms re-deposit back onto the surface, may have occurred and this may have resulted in an increased N level. Although the Ti and N levels were consistent throughout the substrate, as with the ZrN film, the N content remained high for at least 6 μm. Analysis of the data in table 4-3 (depth = 9.2 μm) revealed a Ti:N substrate ratio of 3.77. While this ratio was greater than that for the ZrN coated disc, the N level in the TiN coated substrate was far greater than the maximum
allowable amount (0.05 wt%). This Ti/N ratio of 3.77 suggests a N content of 21 at%. The solubility limit of N in pure Ti, according to the Ti-N equilibrium phase diagram, is equal to 15 at% at 600 °C. This may explain the steady and flat N diffusion zone in the first 6 μm of the Ti alloy substrate. Again, this result indicated rapid diffusion of N into the substrate during the coating process. Comparing figure 4-26 to 4-27, it could be seen that the change in the relative atomic % of N, from the TiN film to the substrate, was greater than that for the ZrN film. This may have been why the EDX linescan for the TiN film showed a change in the N level across the film/substrate interface, while the linescan for the ZrN film did not.

![Graph showing relative atomic % vs. depth into TiN film for O, Ti, N, and C.](image)

**Figure 4-27.** Relative atomic % vs. Depth into TiN film for O, Ti, N, and C.

<table>
<thead>
<tr>
<th>Depth (μm)</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
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<td>15.28</td>
<td>24.41</td>
<td>39.26</td>
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<td>56.04</td>
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</tr>
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<td>57.0</td>
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<td>20.21</td>
<td>29.13</td>
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<tr>
<td>9.2</td>
<td>7.15</td>
<td>73.41</td>
<td>19.43</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Table 4-3.** Relative atomic % of elements in TiN film.
XPS depth profiling was performed on the amorphous carbon coating in an attempt to identify the composition of the two layers and figure 4-28 represents a plot of relative atomic % versus depth into the AC coated specimen for oxygen, titanium, nitrogen, and carbon. The relative amount of each element at various depths beneath the AC surface can be found in table 4-4. As with the TiN and ZrN films, the surface of the AC film contained a thin oxide layer which was removed immediately after sputtering began.

![Amorphous Carbon](image)

**Figure 4-28.** Relative atomic % vs. Depth into AC film for O, Ti, N, and C.

<table>
<thead>
<tr>
<th>Depth (μm)</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>21.0</td>
<td>4.2</td>
<td>3.53</td>
<td>71.27</td>
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<td>0.6</td>
<td>6.34</td>
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<td>1.2</td>
<td>5.22</td>
<td>13.74</td>
<td>5.35</td>
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<td>1.8</td>
<td>5.33</td>
<td>47.58</td>
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<td>2.1</td>
<td>9.14</td>
<td>44.26</td>
<td>16.59</td>
<td>30.1</td>
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<td>2.7</td>
<td>4.98</td>
<td>47.34</td>
<td>47.68</td>
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</tr>
<tr>
<td>3.3</td>
<td>3.54</td>
<td>40.54</td>
<td>53.57</td>
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</tr>
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<td>4.2</td>
<td>11.65</td>
<td>66.94</td>
<td>21.41</td>
<td>0.0</td>
</tr>
</tbody>
</table>
From figure 4-28, it can be seen that the amorphous layer, which was identified to be approximately 2 μm thick (Fig 4-12), was comprised mostly of carbon but did contain a small amount of titanium. The carbon level was highest near the surface and slowly decreased throughout the amorphous layer until approximately 1.5 μm, where it experienced a sharp drop. Between 1.8 and 2.2 μm below the surface, the carbon content leveled off while the Ti and N levels rose. This 0.4 μm thick region represented the interface between the amorphous and columnar layers and consisted of titanium (46%), nitrogen (16%), and carbon (30%). Beneath this diffusion zone, the carbon level fell sharply to zero, the nitrogen level rose, and the titanium content remained constant. The next 1.6 μm, from 2.2 to 3.8 μm, represented the columnar layer of the AC film and it was evident from the XPS data that this layer was TiN. These results were consistent with the EDX linescan presented in figure 4-25b. At a depth of 3.8 μm, the nitrogen level dropped off sharply while the Ti content rose to approximately 65%. This result indicated that the film had been traversed and that the substrate was being sampled.

Unfortunately, profiling was stopped at this point and the diffusion of N into the substrate could not be investigated. However, from figure 4-28, it appeared that the nitrogen content leveled off between 10 and 20 % and, while this was lower than the substrate N levels in the TiN and ZrN films, it was still more than the maximum N content in the Ti6Al4V alloy. Again, this suggested diffusion of N into the substrate during the coating process.
5.0 RESULTS AND DISCUSSION - Fretting Tests

5.1 UNMODIFIED Ti6Al4V

Two unmodified Ti6Al4V control specimens were included in each of the three fretting experiments and the resulting surface damage, assessed using scanning electron microscopy and non-contact profilometry, was found to be consistent from specimen to specimen. The following description of those specimens illustrates that adhesive galling was the predominant wear mechanism and that the fretting behaviour of the unmodified control specimens was characterized by material transfer and a significant increase in surface roughness.

5.1.1 Scanning Electron Microscopy

Test surfaces were examined at a 55° tilt angle using secondary electrons and accelerating voltages of 10 and 15 KeV. Figure 5-1 is an electron micrograph of an unmodified Ti6Al4V specimen which had been fretted against a Co-alloy sphere for 240,000 cycles. Unexpectedly, two distinct fretting scars existed; indicating lateral displacement of the cobalt alloy sphere during testing. This was most likely caused by accidentally moving the load arm during temperature or pH measurements. As the test employed a sphere on flat configuration, the elliptical shape of the upper scar suggested continuous lateral movement of one of the specimens throughout the test. It was believed that misalignment of the half wedges (sec 3.3.1) caused a small rotation of the linear bearing and a slight lateral movement of the Ti6Al4V flat.

Examination of the unmodified specimen at higher magnifications (Fig 5-2) suggested that the predominant wear mechanism was adhesive galling. This type of wear, characterized by roughened surfaces and abundant material transfer, involves micro-welding between surface asperities which are, subsequently, sheared and plucked away. The extracted material is often re-deposited onto the original surface and the resulting increased surface roughness may lead to an increased rate of wear. Evidence of material transfer could be seen in figure 5-3. In contrast to figure 5-1, the fretting scar found in figure 5-4 was circular in shape, indicating proper maintenance of specimen positioning throughout the test. The fretting scar was surrounded by a ring of non-conducting material, and contained a relatively small amount of surface damage. Through EDX analysis, this non-conducting material was identified as a Ti and/or Cr oxide. Approximately 1/4 of the fretted area exhibited evidence of surface damage and it was interesting to note that the oxide was absent throughout this area. This suggested that oxide deposition and removal may have contributed to the subsequent surface damage as a result of a third-body wear mechanism.
Figure 5-1. Fretting scars on unmodified specimen. Two scars indicated specimen movement in the lateral direction.

Figure 5-2. High mag. image of unmodified Ti surface.
Figure 5-3. Evidence of material transfer.

Figure 5-4. Unmodified Ti fretting scar. Note the absence of the Cr-rich oxide in the damaged area.
Although this scar appeared quite different from those seen in figure 5-1, examination at higher magnifications revealed that the three were quite similar. Figure 5-5 is an electron micrograph of both the damaged and undamaged surfaces of the circular scar seen in the previous figure. The area from which this micrograph was taken is marked by the black box (Fig 5-4) and both surfaces had been in contact with the cobalt sphere. From figure 5-5, it was apparent that material had been ripped away from the unmodified surface and that adhesive wear was the predominant mechanism. This was further supported by the presence of material which appeared to have been re-deposited onto the Ti alloy surface (Fig 5-6).

While the fretting scars generated by the six control specimens did not always appear the same, examination at higher magnifications consistently revealed evidence of adhesive wear and material transfer. These findings were consistent with the results of the profilometry studies which are presented in the following section.

![Image](image.png)

Figure 5-5. Interface between damaged and undamaged surfaces. Micrograph shows evidence of adhesive wear.
5.1.2 Non-Contact Profilometry

In efforts to obtain information on the size, shape, and depth of the fretting wear scars, test specimens were examined with a WYKO profilometer. The test surfaces were examined in the VSI (vertical scanning interferometric) mode at a magnification of 10.2 X. All specimens were positioned such that the fretting direction was parallel to the long axis of the X-profile (See Fig 5-7a).

As previously mentioned, the initial average surface roughness (Ra) of the unmodified control specimens was equivalent to 0.027 μm (table 4-1). Following testing, this value increased to 0.16 μm. This large increase in surface roughness was a direct result of adhesive galling and the transfer of material associated with it. Evidence supporting this can be seen in the following figures.

Surface profiles, in the x and y directions, of a representative unmodified Ti6Al4V fretting scar can be seen in figures 5-7a and 5-7b, respectively. The two profiles indicated that the unmodified surfaces experienced both positive and negative wear; consistent with the adhesive galling mechanism previously described. Close examination of figure 5-7b revealed that the maximum damage protruded approximately 1 μm into the surface and that deposition of material was more common at, but not limited to, the edges of the contact.
circle. All six control specimens showed evidence of both positive and negative wear and possessed increased Ra values.

Further evidence of adhesive galling and the transfer of material was obtained by examining the cobalt alloy counter-surfaces. Again, the x and y surface profiles of a representative cobalt alloy sphere can be seen in figures 5-8a and 5-8b, respectively. Both figures indicated that a large amount of material had been transferred, presumably, from the unmodified titanium alloy surface to the cobalt alloy sphere. While the transferred material could not be identified with the profilometer, the absence of any significant surface damage to the sphere dismissed any suggestion that the material was metallic cobalt. Although cobalt based oxides may have been present, it was believed that the bulk of this material was Ti based. As previously mentioned, these results were representative and while some of the spheres did not exhibit such pronounced material transfer, all counter-surfaces were characterized by minimal surface damage and some material transfer.

Mag : 10.2 X

X-Profile

Fretting Direction

Y-Profile

Figure 5-7. Surface profiles of unmodified Ti6Al4V fretting scar.

Mag : 10.2 X

X-Profile

Y-Profile

Figure 5-8. Surface profiles of Co sphere fretted against unmodified Ti6Al4V.
5.1.3 Single Pass Test

In efforts to obtain information on the wear mechanism(s) responsible for the previously described surface damage, a fourth fretting test was conducted. Visual inspection of the unmodified Ti6Al4V surface following this test revealed slight surface damage which appeared to be the result of small abrasive scratches. Examination with the SEM implicated another type of wear, however, and micrographs of the fretted surface can be found in figures 5-9 and 5-10.

As opposed to the scars seen earlier (Fig 5-1 and Fig 5-4), the surface damage resulting from the single pass test did not possess any distinct shape nor could the contact circle be distinguished (Fig 5-9). Evidence of material which had been plucked from, and smeared over, the unmodified surface could be seen and the resulting surface damage was consistent with that produced from adhesive galling. Figure 5-10 is a high magnification micrograph taken at the outer edge of the damaged area and exhibits a piece of material which had been partially removed from the unmodified surface. Cracks running into the undamaged surface could be seen and it was believed that this portion of the surface was in the process of being removed through an adhesive wear mechanism. It should be noted that there was no evidence of abrasive wear.

![Figure 5-9: Surface damage produced from one fretting cycle.](image)
5.2 TITANIUM NITRIDE (TiN)

5.2.1 Scanning Electron Microscopy
As with the unmodified Ti6Al4V controls, the TiN coated specimens were examined at a 55° tilt angle using secondary electrons. Representative micrographs can be seen in figures 5-11 and 5-12. Analogous to figure 5-4, both fretting scars were circular in shape and were surrounded by a ring of non-conducting material. EDX mapping identified this material as a chromium-rich oxide (Fig 5-13). Unlike the unmodified Ti6Al4V surfaces, the TiN coated specimens exhibited no evidence of significant wear. There were no signs of coating failure, delamination, or surface scratching. In fact, a slight increase in surface roughness was the only effect fretting had on these coatings.

5.2.2 Non-Contact Profilometry
After fretting, the average surface roughness of the TiN coated specimens increased slightly, from 0.046 µm to 0.08 µm, as a result of the Cr-rich oxide which had been deposited onto the surface. Although almost double their initial value, the roughness of the fretted TiN surfaces was well below that of the fretted unmodified controls (0.16 µm).
Figure 5-11. Fretting scar on TiN surface. Scar is surrounded by ring of oxide material.

Figure 5-12. Fretting scar on TiN surface. Oxide is more dispersed.
Figure 5-13. EDX mapping of Cr oxide debris on TiN surface (Approx. 2400x).

As previously mentioned, the TiN fretted surfaces were characterized by minimal wear and the deposition of a chromium-rich oxide. Representative profiles of the fretted TiN surfaces, found in figures 5-14a and 5-14b, supported this. In figure 5-14b, the oxide ring was represented by the two small spikes positioned at approximately 100 µm and 300 µm and, while the oxide ring was less defined in the x profile, it could be seen that the TiN coating experienced primarily positive wear (i.e. the deposition of material onto the surface). As the deep spike found in figure 5-14b was outside the contact area, it was dismissed as a defect in the TiN film.

The x and y surface profiles of a representative cobalt alloy sphere which had been fretted against TiN can be seen in figures 5-15a and 5-15b, respectively. Unlike the unmodified Ti6Al4V controls, the TiN films had a deleterious effect on the counter-surfaces. While significant material transfer was absent, abrasion and damage to the counter-surfaces did occur; large grooves and deep scratches on the surface of the sphere could be seen in both figures. For comparison, the profiles of an unfretted cobalt alloy sphere are presented in figure 5-16.
Mag : 10.2 X

X-Profile

Y-Profile

Figure 5-14. Fretted surface of TiN coated specimen.

Mag : 10.2 X

X-Profile

Y-Profile

Figure 5-15. Profiles of cobalt counter-surface fretted against TiN.

Mag : 10.2 X

X-Profile

Y-Profile

Figure 5-16. X and Y profiles of an unfretted Co-alloy sphere.
5.2.3 Single Pass Test

No evidence of surface damage or the deposition of oxide material was observed for the TiN film. This was the expected result given the lack of surface damage and the relatively small amount of oxide deposited onto the TiN surface after prolonged fretting.

5.3 ZIRCONIUM NITRIDE (ZrN)

5.3.1 Scanning Electron Microscopy

Analogous to TiN, the fretting behaviour of the ZrN coating was characterized by minimal wear and a slight increase in surface roughness. Electron micrographs representative of the fretted ZrN surface can be found in figures 5-17 and 5-18. As with the TiN film, both fretting scars were circular in shape and contained a large amount of non-conducting material. Again, EDX analysis identified this material as a chromium rich oxide (Fig. 5-19). In contrast to the TiN film, the oxide material was not deposited as a ring but dispersed evenly throughout the fretted ZrN surface. The reasons for this are unknown; however, one possible explanation is that the Cr oxide was more strongly bonded to the ZrN film than to the TiN film. This well-adhered oxide would resist fragmentation and accumulation at the edges of the contact circle and remain distributed evenly throughout the fretted area. It is possible that Zr has a greater affinity for Cr than Ti and, while no information could be found in the literature, a well-adhered Cr oxide could be the result.

5.3.2 Non-Contact Profilometry

Much like the TiN film, the ZrN coatings experienced a slight increase in surface roughness from 0.045 μm to 0.07 μm attributable to the build-up of oxide material. Representative profiles of the ZrN fretted surface, in the x and y directions, can be seen in figures 5-20a and 5-20b, respectively. The large upward spikes, located near the centre of each figure, represent the fretted area and the deposition of material. The spikes which protrude into the surface of the film, including the deep one at 110 μm (Fig. 5-20b), were likely associated with defects in the ZrN film.
Figure 5-17. ZrN fretting scar. Oxide ring is less pronounced.

Figure 5-18. ZrN fretting scar showing well-dispersed oxide material. Little surface damage is seen.
Given the similarities between the fretting behaviour of the ZrN and TiN films, it was not surprising that the performance of the counter-surfaces was also very similar. The surface profiles of a representative cobalt alloy sphere which had been fretted against ZrN can be seen in figures 5-21a and 5-21b. As with those fretted against TiN, the ZrN counter-surfaces experienced abrasive wear and possessed significantly rougher surfaces.

Mag : 10.2 X

**Figure 5-20.** Surface profiles of fretted ZrN surface.
5.3.3 Single Pass Test

No evidence of surface damage was observed for the ZrN film after the single pass fretting test. Again, this was the expected result as the ZrN coating exhibited an excellent resistance to fretting over a quarter of a million cycles. Although the ZrN films contained more oxide debris than the TiN films throughout the extended fretting experiments, no evidence of oxide was present on the ZrN surface after the single pass test.

5.4 AMORPHOUS CARBON (AC)

Experimentation with the amorphous carbon films produced the most interesting results. In total, six AC coated specimens were tested and, surprisingly, three showed extensive fretting damage to the AC film, with large wear scars being generated. These scars were consistent in size, shape, and depth. The fretting behaviour of the three specimens which didn’t fail was characterized by slight polishing wear and flattening of surface asperities.

5.4.1 Scanning Electron Microscopy

As previously mentioned, all of the three failed AC specimens produced near identical fretting scars in terms of size, shape, and depth. The surfaces of the failed specimens were not consistent, however, as two exhibited evidence of abrasive wear and excessive scratching, while the third was scratch free. An electron micrograph of one of the failed specimens which experienced abrasive wear can be seen in figure 5-22. In addition to the small scratches which ran parallel to each other, a large, severely damaged region was observed near the centre of the scar. While the presence of such severe surface
damage may have been unexpected, its location was not as this area experiences the largest contact stresses.

While the wear process was abrasive in nature, examination of the scar at higher magnifications suggested the source of the abrasive particles. Figure 5-23 is an electron micrograph of the heavily damaged central region and, from it, it appeared that fragments of the film were removed through an adhesive wear or coating fracture mechanism. The generation of particulate matter through either mechanism would be detrimental to the coating’s wear resistance, particularly if the abrasive particles could not escape the contact circle. Therefore, it is of utmost importance that a coating possesses high cohesive strength and resists fragmentation.

The surface damage at the edge of the AC fretting scar was characterized by shallow scratches and small U-shaped cracks. These cracks, seen in figures 5-24 and 5-25, were somewhat unexpected as this area experienced the smallest contact stresses. Several of these cracks could be seen, including one at the outermost edge of the contact circle where the stresses were near zero (Fig 5-24). The material within the ‘U’ appeared to dip down, exposing the microstructure of the amorphous carbon layer (Fig 5-26). The presence of these cracks may have been related to fatigue failure of the coating and suggested poor film cohesion. While these features may have been evidence of initial coating failure, the peculiar shape of these surface cracks could not be explained.

Figure 5-22. Amorphous carbon coating exhibiting extensive fretting damage.
Figure 5-23. Micrograph of central region. Adhesive wear or coating fracture appears to be responsible for coating failure.

Figure 5-24. Small ‘U’ shaped cracks present on AC surface near the outer edge of the fretting scar.
Figure 5-25. High magnification of surface crack.

Figure 5-26. Material in the centre of the crack appears to dip down. Microstructure of upper amorphous carbon layer can be seen.
The fretting scar of the third failed AC coating can be seen in figure 5-27. While this scar had dimensions comparable to those scars previously described, very little evidence of surface wear existed. Apart from the two deep pits which showed some evidence of abrasion, the majority of this surface was scratch-free. Figure 5-28 is an electron micrograph taken at the edge of the fretting scar and, from it, it can be seen that the fretted surface was relatively smooth and free of damage; no U-shaped cracks were observed. The marked difference in surface damage between this fretting scar and the one representative of the other two failed specimens could not be explained; however, examination with the profilometer revealed that all three scars possessed nearly identical dimensions.

The fretting performance of the three AC specimens which did not exhibit extensive fretting was quite different. As previously mentioned, these specimens experienced slight polishing wear and a representative fretting scar can be seen in figure 5-29. No evidence of coating failure, cracks, or surface damage was observed. In fact, the only effect fretting had was a darkening of the film believed to be caused by flattening of the surface asperities.

![Figure 5-27. Fretting scar of third failed AC coating. Note the absence of abrasive scratches.](image-url)
Figure 5-28. Edge of fretting scar seen in previous figure.

Figure 5-29. Fretted surface of an AC coating which experienced slight polishing wear.
5.4.2 Non-Contact Profilometry

Surface profiles of the wear scars found in figures 5-24 and 5-28 can be seen in figures 5-30 and 5-31, respectively. As previously mentioned, both scars were of similar size, shape, and depth, with an average diameter of approximately 275 μm. The maximum depth of each scar was slightly more than 4 μm, indicating that the coatings may have been breached and the underlying substrates may have been exposed. Another important observation was that, with the exception of the deep holes at the centre, the average depth of each scar was approximately 2 μm. This was equivalent to the thickness of the upper amorphous carbon film and may suggest poor adhesion between the two layers.

Representative surface profiles of the three coatings which experienced polishing wear can be seen in figures 5-32a and 5-32b. No evidence of surface damage was observed and the sharp peak seen in both profiles was likely caused by a foreign particle present on the AC surface during examination. Unlike the two nitride films, oxide material was absent from the carbon surface. For the coatings which failed, this was not unexpected as the oxide would have been consumed throughout the wear process; however, the absence of an oxide on the three carbon films which did not fail was a surprise.

All of the Co-alloy spheres which had been fretted against the AC coated specimens experienced some form of surface damage, regardless of whether the coating failed or not. Representative surface profiles of spheres fretted against coatings which didn’t fail, and those which did, can be seen in figures 5-33 and 5-34, respectively. The difference between the two was primarily in the severity of the surface damage. Fretting against a coating which didn’t fail produced mild to moderate wear (Fig 5-33); whereas, fretting against coatings which did fail resulted in surface damage comparable to that produced by the nitride films (Fig 5-34).

Mag : 10.2 X

![X-Profile](image-url) ![Y-Profile](image-url)

**Figure 5-30.** Profiles of fretting scar generated on a amorphous carbon coating which experienced abrasive wear (Fig 5-22).
Mag : 10.2 X
X-Profile

Y-Profile

Figure 5-31. Surface profiles of deep fretting scar produced on a AC surface which did not show signs of abrasive wear (Fig 5-27).

Mag : 10.2 X
X-Profile

Y-Profile

Figure 5-32. Surface profiles of AC coating which experienced polishing wear.

Mag : 10.2 X
X-Profile

Y-Profile

Figure 5-33. Cobalt sphere fretted against AC coating which experienced slight polishing wear.
5.4.3 Single-Pass Test

No evidence of coating failure could be found on the AC surface after it had experienced a single fretting cycle. As only half of the carbon coatings failed, this result was somewhat expected. While those coatings which didn’t fail experienced slight polishing wear, as identified by a darkened surface, no evidence of polishing or darkening of the film’s surface was observed after the single pass test. These results suggested that the failure of the three AC films was time-dependent and possibly related to a coating fatigue mechanism.

5.5 ZIRCONIUM OXIDE (ZrO$_2$)

5.5.1 Scanning Electron Microscopy

As with the carbon film, experimentation with the sol-gel-formed zirconium oxide coatings produced some interesting results. Of the three coatings tested, two failed and produced large fretting scars characterized by severely roughened surfaces. Figure 5-35 exhibits an electron micrograph of one of the failed coatings and it can be seen that the fretting scar produced was much larger than any previously seen. Analogous to the nitride films, the ZrO$_2$ fretting scars were surrounded by a ring of non-conducting material and, again, EDX analysis identified it as a chromium-rich oxide (Fig 5-37).

Similar to the fretting scars produced on the three failed AC coated specimens, the centre of the ZrO$_2$ coating experienced the most severe damage. This central area endured high contact stresses and examination at higher magnifications revealed evidence of both abrasive and adhesive wear mechanisms. Long parallel scratches and small surface pits could be seen throughout the fretted area (Fig 5-36). At the outer regions of the scar,
where the contact stresses were low, small abrasive scratches were observed, the film was smooth, and evidence of adhesive wear was absent (Fig 5-38). This result suggested that, in these low stress areas, the coating experienced abrasive wear caused by trapped ZrO₂ particles. No evidence of coating delamination was observed and the high shear adhesion strengths previously exhibited by this sol-gel ZrO₂/Ti6Al4V system suggested that cohesive failure of the underlying substrate was responsible for the production of third body abrasives. Cohesive failure of the substrate would produce ZrO₂ coated debris and account for the adhesive wear observed at the centre of the fretting scar. The sol-gel ZrO₂ coating may have been too thin to shield the Ti6Al4V alloy from the high contact stresses and adhesive galling may have occurred despite the fact that the surface was modified.

The fretting behaviour of the ZrO₂ coating which didn’t fail was characterized by minimal surface damage and the deposition of Cr-rich oxide (Fig 5-39). This fretting scar had an appearance similar to the scars produced by the ZrN film.

Figure 5-35. Large fretting scar produced on ZrO₂ surface.
Figure 5-36. Heavily damaged central region of ZrO$_2$ scar. Micrographs shows evidence of abrasive and adhesive wear.

Figure 5-37. EDX mapping of oxide particle on ZrO$_2$ surface (Approx. 1500x).
Figure 5-38. Parallel scratches observed at the outer edge of the ZrO₂ fretting scar.

Figure 5-39. Surface of undamaged ZrO₂ film. Deposition of Cr-rich oxide was only effect of fretting.
5.5.2 Non-Contact Profilometry

From table 4-1, it can be seen that, prior to testing, the zirconia film had the best surface finish. In fact, the roughness of the ZrO₂ film was comparable to that of the polished substrate. Following fretting, however, the average surface roughness of the ZrO₂ films which had failed increased significantly from 0.025 μm to 0.36 μm. The ZrO₂ specimen which didn’t fail experienced only a slight increase in surface roughness from 0.025 μm to 0.032 μm.

The surface profiles of two ZrO₂ coated specimens, one which failed and one which didn’t, can be found in figures 5-40 and 5-41, respectively. Figures 5-40a and 5-40b exhibited a very rough surface characterized by both positive and negative wear. The surface damage protruded to a maximum depth of approximately 1.5 μm, indicating that the film had been breached and the substrate exposed. The zirconia film which didn’t fail showed no evidence of failure or surface damage.

Examination of the Co-alloy counter-surfaces produced an unexpected result. Figures 5-42a and 5-42b are the surface profiles of a Co-alloy sphere which had been fretted against one of the zirconia coated specimens which had failed. From this figure, it could be seen that the counter-surface was completely destroyed and flattened. This was unquestionably the result of ZrO₂ particles remaining within the contact circle and participating as third body abrasives. This result also helps to explain why the fretting scars of the two failed zirconia samples were so large. Such severe damage to the counter-surfaces was unexpected and illustrated the importance of using a coating with good film/substrate adhesion and strong film cohesion. The profile of the Co sphere which was fretted against the ZrO₂ specimen which didn’t fail experienced very mild wear and a small amount of flattening at the tip.

Mag : 10.2 X

![X-Profile](A) ![Y-Profile](B)

Figure 5-40. Profiles of a failed ZrO₂ surface (Fig 5-35).
5.5.3 Single Pass Test

As with the other films, no evidence of surface damage or deposition of an oxide was observed for the ZrO₂ film. Unlike the three PVD films, this result was not totally expected as two of the three ZrO₂ coated specimens failed during the extended fretting experiments. While the sol-gel-formed ZrO₂ coating was hard and possessed high film/substrate shear adhesion strengths, it was thought that some abrasive scratches may have developed during the single pass test. The absence of such scratches indicated that the abrasive wear exhibited by the two failed coatings (Fig 5-35 and Fig 5-37) was the result of substrate failure and the entrapment of ZrO₂ coated particulate debris.
6.0 SUMMARY AND CONCLUSIONS - Material Characterization

6.1 TITANIUM NITRIDE (TiN)

Coating with the TiN film resulted in a large increase in surface roughness attributed to defects developed during the coating process. Macroparticles, pinholes, and other, larger, defects were observed throughout the TiN surface and, while some of these defects appeared to expose the substrate, it was believed that the majority of them did not. The TiN coating was found to be uniform and approximately 3 μm thick with a dense columnar structure, typical of a zone T microstructure. EDX studies suggested that an Al and Ti deficient zone existed just below the film/substrate interface and XPS depth profiling revealed an increased level of N throughout the substrate. This N rich zone existed for at least 3 μm and was most likely due to nitrogen diffusing into the substrate during the coating process.

6.2 ZIRCONIUM NITRIDE (ZrN)

As with the TiN film, the surface roughness of the ZrN coating was nearly double that of the underlying substrate and this, too, was attributed to defects present on the film’s surface. The ZrN coating had a thickness of 3 μm, was uniform, and possessed a columnar, zone T microstructure. Unlike the TiN film, small cracks were discovered on the fractured surface of the ZrN film; indicating, perhaps, an increased film density. Examination of the fractured surface also suggested the existence of a thin intermediate layer between the ZrN film and the substrate; however, no evidence of this could be found through EDX or XPS studies. The X-ray studies did produce some unexpected results, however, as EDX surface and linescans insinuated that the ZrN film was, essentially, void of nitrogen. Only a small N peak was present on the surface spectrum and no change in the N level was observed across the film/substrate interface during the linescan studies. XPS depth profiling revealed that the ZrN film possessed an abundant amount of N and that, like the TiN coating, the nitrogen level remained high for at least 6 μm into the substrate. Again, diffusion of N during the coating process was thought to be responsible.
6.3 AMORPHOUS CARBON (AC)

The carbon film had the greatest surface roughness, however, unlike the two nitride films, this was not attributable to defects but to a film surface texture. While this coating did appear to have a few shallow pits or holes, macroparticles were absent and the quality of the carbon coating appeared quite good. The AC coating was multi-layered and, while each layer was approximately 2 μm thick, they differed significantly in structure. The upper layer was amorphous while the intermediate one, like the nitride films, had a columnar structure. It was believed that the intermediate layer was introduced to improve the adhesion of the carbon film to the substrate; however, large portions of the AC coating were removed during edge polishing, an effect that was not seen with the other coatings. EDX surface and linescan analysis suggested that the intermediate layer was comprised of TiN and XPS depth profiling verified this. The upper layer was almost entirely carbon and a 0.4 μm thick diffusion zone existed between the two layers. While profiling was not continued into the substrate, it appeared that an increased level of N below the film/substrate interface did exist.

6.4 ZIRCONIUM OXIDE (ZrO₂)

A direct result of the sol-gel dipcoating process was a ZrO₂ film with a surface roughness equivalent to that of the Ti6Al4V substrate. Two types of defects were associated with this film, long interconnected cracks, found in areas of increasing film thickness, and small ‘diamond’ shape cracks, resulting from contaminants present on the substrate surface prior to coating. The quality of the sol-gel-formed films used in the present study was quite good as only a few cracks were observed. Unlike the PVD coatings, the thickness of the sol gel film was not uniform and increased towards the edges of the modified disc. The thickness of the ZrO₂ film at the centre of the disc, where the fretting experiments took place, was equivalent to 100 nm. A consequence of small film thickness is the excitation of both the coating and the substrate during x-ray studies. As expected, the EDX surface spectrum exhibited peaks corresponding to O, Zr, Ti, Al, and V.
7.0 SUMMARY AND CONCLUSIONS - Fretting Tests

7.1 UNMODIFIED Ti6Al4V

While the size and shape of the wear scars differed from specimen to specimen, each fretting scar was rough and contained material which had been re-deposited onto the unmodified surface. Evidence of material transfer from the unmodified Ti alloy discs to the Co alloy spheres was evident in the non-contact profilometry studies and damage to the counter-surfaces was insignificant. These same studies revealed that the unmodified surfaces experienced both positive and negative wear and that the surface damage protruded to a maximum depth of approximately 1 μm. The single fretting cycle test revealed that the predominant wear mechanism was adhesive in nature and that the central, high contact stress area was damaged first.

The unmodified surfaces experienced adhesive galling and the resulting damage was characterized by roughened surfaces and abundant material transfer.

7.2 NITRIDE FILMS (TiN and ZrN)

Evidence of surface wear, damage, or coating failure could not be found on any of the nitride films and the only effect fretting had was the deposition of a Cr-rich oxide. This oxide material was deposited as a ring on the TiN surface and, while it was more evenly dispersed on the ZrN film, its presence led to a slight increase in surface roughness on both films. The profilometry studies revealed that Co-alloy spheres, fretted against TiN and ZrN, experienced a significant amount of surface damage as a result of abrasive wear. The spherical counter-surfaces exhibited large, deep scratches and severe surface roughening. No surface damage was produced during the single pass test and both films exhibited an excellent resistance to fretting. To summarize:

The fretting behaviour of the TiN and ZrN films was characterized by minimal surface damage and the deposition of oxide material. No evidence of coating failure or delamination was observed and both coatings appeared to be highly resistant to fretting.
7.3 AMORPHOUS CARBON (AC)

The fretting behaviour of the six AC coated specimens was characterized by either slight polishing wear or complete coating failure. Polishing wear, occurring in three cases, was identified by a darkening of the film and evidence of surface damage or oxide deposition was non-existent. The Co spheres fretted against these AC coatings experienced only a slight increase in surface roughness and minor abrasive scratching.

The three failed AC coatings produced large, deep wear scars identical in size, shape, and depth. The centre of each scar contained a deep pit which protruded down through the thickness of the film exposing the substrate. Examination of this heavily damaged central region indicated that the coating had experienced cohesive failure and that coating fragmentation had resulted in abrasive wear. The appearance of small U-shaped cracks on the outer, low stress regions of the fretting circle provided further evidence of cohesive failure. The Co spheres fretted against these failed AC coatings possessed surface damage comparable to that produced by the nitride films. The single pass test produced no observable surface damage.

Poor film cohesion was believed to be responsible for the large, deep fretting scars produced on the failed AC coated specimens. The fretting behaviour of the coatings which didn’t fail was excellent and, while the inconsistency between the two could not be explained, it may have been related to the coating process.

7.4 ZIRCONIUM OXIDE (ZrO₂)

Large fretting scars, exhibiting evidence of both abrasive and adhesive wear, were produced on two of the three ZrO₂ coated specimens. These scars were surrounded by a ring of Cr-rich oxide and possessed a severely damaged central area. The Co spheres fretted against these specimens experienced an extraordinary amount of damage as a result of ZrO₂ coated particles trapped within the contact circle. While the specimen which didn’t fail exhibited a large amount of oxide material, it was evenly dispersed across the fretted area and no evidence of surface damage was observed. The damage to the Co sphere which had be fretted against this specimen was minimal and no evidence of wear or oxide deposition was observed after the single fretting cycle test.

As no evidence of delamination was observed, it was believed that cohesive failure of the substrate was responsible for the large ZrO₂ fretting scar. Experimentation with this film demonstrated the importance of good coating/substrate adhesion and strong film cohesion.
7.5 OVERALL CONCLUSIONS

The need for improved fretting resistance of Ti6Al4V is apparent when the cobalt/unmodified titanium fretting couple is examined. While this titanium alloy has the necessary mechanical properties, biocompatibility, and corrosion resistance to be used in implant applications, its poor wear properties limit its use. This fact was demonstrated by the abundant material transfer and severe surface damage produced during fretting. Surface modification represents an attractive alternative to material substitution or improved implant design and the excellent fretting resistance exhibited by the TiN and ZrN coatings is an example. Many of the coating’s properties are determined by the specific coating process and its conditions and important properties include film/substrate adhesion, hardness, residual stresses, and film cohesion. The breakdown of the amorphous carbon film, which used an intermediate layer to bond it to the substrate, may have suggested poor film adhesion; however, it was more likely related to poor film cohesion and the ability of cracks to develop on the surface of the film. Excellent film/substrate adhesion and strong film cohesion doesn’t ensure good fretting resistance, however, as was discovered with the sol-gel-formed ZrO2 coating. This coating failed, possibly, through cohesive failure of the underlying substrate and, in such a case, other coating properties such as thickness, defect density, and fracture toughness become important.

While improving the fretting resistance of the titanium-alloy was the primary objective of this study, the cobalt-alloy counter-surfaces cannot be overlooked. Improving the wear resistance of the Ti component, at the expense of the Co component, is undesirable as the generation of any particulate debris (Ti or Co) in vivo could pose a severe effect to the host and undermine the success of the implant. For this reason, the sol-gel-formed zirconia coating must be optimized before it can be considered as a viable solution to this fretting corrosion problem as the release of particulate debris by this film severely damaged the counter-surfaces.

Recommendations which can be made based on this study are to continue testing, perhaps in environments and under conditions which more closely simulate the in vivo environment, with the nitride films (TiN and ZrN) as these coatings appear to possess good film/substrate adhesion and an excellent resistance to fretting. Both the amorphous carbon and sol-gel films must be optimized before they can be considered for any further testing.
REFERENCES


42. S.J. Bull, Correlation of microstructure and properties of hard coatings, *Vacuum*, Vol. 43 (No. 5-7), p 387, 1992


8.0 APPENDIX A: Polishing Ti6Al4V Specimens

The following protocol was used for polishing the titanium alloy discs substrates. All discs were cut from Ti6Al4V ELI bar stock and polished using an automated polishing unit (AUTOMET*2 Power Head, Buehler, Lake Bluff, IL). The discs were mounted in bakelite (red phenolic powder, Buehler, No. 20-3200-080) and cured at 150 °C and 30 Mpa for 8 minutes in a mounting press (Pr-10, Leco Corp., St. Joseph, MI). All discs were cooled in the press for 20 minutes before being removed.

8.1 Automated Polishing Protocol

1. Specimens were ground flat using silicon carbide papers (Carbimet, No. 30-5108-240, -320,-400,-600, Buehler). Settings for the automated polishing unit were as follows: lubricant - water; speed - 240 rpm; load - 5 lbs/sample*; sample rotation - same direction as the abrasive wheel (comp). With the exception of initial grinding, grinding time increased by 15 sec for every paper starting at 1 min for the 320 grit paper. Initial grinding, with the 240 grit paper, lasted between 1-2 min. or until the specimens were planar (as indicated by a uniform scratch pattern).

2. Between each step, specimens were rinsed with distilled water and dried with forced filtered air.

3. Ultra fine silicone carbide papers (MICROCUT, No. 30-5528-800, -012, Buehler) were used to grind the discs to 800 and 1200 grit finishes, respectively. The conditions used for the automated polishing unit are those as described in (1). The time for grinding at the 800 and 1200 papers was 1.5 minutes and 2.0 minutes, respectively.

4. The samples were cleaned and dried as in 2.

5. Initial polishing was performed with a synthetic rayon cloth (MICRCLOTH, No. 40-7218, Buehler) and a 1.0 μm alumina (Al₂O₃) suspension (MICROPOLISH, No. 40-6354-006, Buehler). The conditions used during this step were as follows: lubricant - distilled water; speed - 120 rpm; load - 7 lbs/sample*; rotation - opposite abrasive wheel rotation (contra); time - 4.0 min. The distilled water was applied as necessary to keep the cloth moist.

6. The specimens were cleaned and dried as in 2.

7. Final polishing employed a 0.06 μm colloidal silica (SiO₂) suspension (MASTERMET, No. 40-6370-064, Buehler) and a CHEMOMET polishing cloth (No. 40-7918, Buehler). The silica suspension was used as the extended lubricant and applied every 30 seconds. Polishing conditions included: speed - 120 rpm; load - 10 lbs/sample*; rotation - contra.
8. The specimens were immediately flushed with water and carefully wiped with a Kimwipe (EX-L, Kimberly-Clark Corp., Roswell, GA).

9. The samples were dried with filtered forced air.

* This is the force per 1 1/2" bakelite mount being polished, not the force of each Ti sample as many of the bakelite mounts contained more than one Ti-alloy disc.
9.0 APPENDIX B: Zirconia Precursor Solution

EQUIPMENT:
- Balance, accurate to 0.01 g
- Stirring plate
- Stirring bar
- Glass beaker, 150 ml
- Beaker lid

CHEMICALS:
- Glacial Acetic Acid, CH₃COOH (ACS grade, ACP Chemicals, Montreal, PQ)
- Zirconium Propoxide, Zr(OCH₃)₄, 70% solution in n-propanol (Johnson Matthey, Ward Hill, MA)
- Double distilled water, ddH₂O
- Ethylene glycol, C₂H₆O₂ (Mallinckrodt, AR)

PROCEDURE:
1. Add 20 g of acetic acid into the beaker and begin to stir.
2. While stirring, add 10 g of the zirconium-propoxide. Stir for an additional two (2) minutes.
3. Maintain stirring, add 6 g of ddH₂O. Stir for an additional ten (10) minutes.
4. Finally, add 3 g of ethylene glycol. Continue stirring for another fifteen (15) minutes.
5. The precursor solution is complete.

ADDITIONAL INFO:
- All sol preparation must be done in a fume hood at room temperature (22 °C).
- The beaker should be kept covered between additions.
- The prepared sol should be stored in a tightly closed jar at room temperature.
10.0 APPENDIX C: Specimen Cleaning and Passivating

10.1 Ultrasonic Cleaning Protocol
1. 2% Decon (BDH Chemicals, Toronto, ON) solution; one (1) hour.
2. Rinse with distilled water.
3. 100% alcohol; thirty (30) minutes.
4. Acetone (AnalaR grade, BDH Chemicals) thirty (30) minutes; repeat with fresh acetone.
5. Dry with filtered forced air.

10.2 Passivation Protocol
1. Passivate in 30% nitric acid (ACS grade, Fisher Scientific) solution, forty (40) minutes.
2. Acetone (AnalaR grade, BDH Chemicals), thirty (30) minutes; repeat with fresh acetone three (3) times.
3. Dry with filtered forced air.

Note: Cleaned and passivated titanium alloy discs which were being treated with the sol-gel process were stored in absolute ethanol (anhydrous, Commercial Alcohols Inc., Brampton, ON) until coating time.
11.0 APPENDIX D: Hank’s Solution Preparation

EQUIPMENT:
- Stirring plate
- Stir bar
- Glass beaker, 1000 ml
- pH meter (PS-15, Corning Inc.)

CHEMICALS:
- Hank’s Balanced Salts powder (cell culture, SIGMA Chemical Corp., St. Louis, MO)
- Low resistivity (16 ??) distilled water, dH₂O (1000 ml)
- Hydrochloric acid, HCl (AnalaR grade, BDH Chemicals, Toronto, ON)
- Sodium hydroxide, NaOH (10N solution, Fisher Scientific)

PROCEDURE:
1. Pour 990 ml of dH₂O into beaker, start stirring.
2. Add Hank’s salt powder while stirring (see note at bottom).
3. Pour 10 ml of dH₂O into Hank’s balanced salt container to get any residual powder.
4. Add to beaker and continue to stir for an additional fifteen (15) minutes.
5. While stirring, buffer Hank’s solution to a pH of 7.3 using the pH meter, HCl, and NaOH.**
6. Transfer buffered solution to a container and seal tightly.
7. Store at room temperature until use.

Note: Salt powder should be added to the dH₂O slowly. A small amount should be added then given time to dissolve before any more is added. Repeat until the salt container is empty.

** Buffering made easier by diluting HCl and NaOH with dH₂O.
12.0 APPENDIX E: Derivation of Maximum Contact Stress

12.1 Calculating Centroids (XX and YY) of the Load Arm

Dimensions of Load Arm

(all dimensions in mm)

<table>
<thead>
<tr>
<th>i</th>
<th>Area ($A_i$)</th>
<th>$x_i$</th>
<th>$y_i$</th>
<th>$A_i x_i$ (mm$^3$)</th>
<th>$A_i y_i$ (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,200 mm$^2$</td>
<td>25</td>
<td>22</td>
<td>55,000</td>
<td>48,400</td>
</tr>
<tr>
<td>2</td>
<td>440 mm$^2$</td>
<td>61</td>
<td>34</td>
<td>26,840</td>
<td>14,960</td>
</tr>
<tr>
<td>3 (hole)</td>
<td>-133 mm$^2$</td>
<td>61.2</td>
<td>34</td>
<td>-8,140</td>
<td>-4,522</td>
</tr>
</tbody>
</table>

$\sum A_i = 2,507 \text{ mm}^2 \quad \sum A_i x_i = 73,700 \text{ mm}^3 \quad \sum A_i y_i = 58,838 \text{ mm}^3 \quad XX = \frac{\sum A_i x_i}{\sum A_i}, \quad YY = \frac{\sum A_i y_i}{\sum A_i}$

The coordinates of the centroid, M, are: $XX = 29.4 \text{ mm}$ and $YY = 23.5 \text{ mm}.$
12.2 Calculating the Maximum Contact Stress

From the previous diagrams, it can be calculated that the distance between the centroid and the centre of the support shaft hole, in the horizontal direction, is 31.8 mm. Knowing that the cobalt sphere is centred in the large block designated as 1, it can be calculated that the distance from the tip of the sphere to the centre of the support shaft hole is equal to 36.2 mm.

The maximum force, F, applied to the sphere by the weight of the arm, L, can be found by taking the sum of the moments around M, the positive direction being counterclockwise. We find:

\[ L(31.8) - F(36.2) = 0 \]

Rearranging,

\[ F(36.2) = L(31.8) \]

Therefore,

\[ F = L(31.8/36.2), \text{ where } L = (\text{mass of arm})(9.81 \text{ m/s}^2) \]

The mass of the arm = 0.817 kg and \( L = 8.0 \text{ N} \)
Therefore, \( F = (8.0 \text{ N})(31.8/36.2) = 7.03 \text{ N} \)

Using the following expression for the maximum Hertzian stress (P):

\[ P_{\text{Max}} = \frac{3F}{2\pi \alpha^2}, \text{ where } \alpha = \left[\frac{((3Fr)/4)(1-v^3)(1/E_1+1/E_2)}{2}\right]^{1/3} \]

\[ r \text{ (radius of sphere)} = 0.00635 \text{ m} \quad E_1 \text{ (Modulus - Ti)} = 110 \text{ GPa} \]
\[ v \text{ (Poisson's ratio)} = 0.33 \quad E_2 \text{ (Modulus - Co)} = 200 \text{ GPa} \]

We find: \( \alpha = 7.49 \times 10^{-5} \) and \( P_{\text{max}} = 598 \text{ MPa} \)

Therefore, the maximum contact stress is at the centre of the contact circle and is equivalent to approximately 600 MPa.
13.0 APPENDIX F: Zirconium Oxide Film Thickness

13.1 Determination of Ns and Ks: Real and imaginary refractive indexes of the substrate material (Ti6Al4V).

<table>
<thead>
<tr>
<th>Ns</th>
<th>Ks</th>
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<tbody>
<tr>
<td>2.2175</td>
<td>3.0517</td>
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<tr>
<td>2.2341</td>
<td>3.0592</td>
</tr>
<tr>
<td>2.2499</td>
<td>3.0658</td>
</tr>
<tr>
<td>2.2474</td>
<td>3.0557</td>
</tr>
<tr>
<td>2.1974</td>
<td>3.0407</td>
</tr>
</tbody>
</table>

Ave. Ns = 2.2293
Ave. Ks = 3.0546

13.2 Determination of ZrO₂ film thickness using Ns and Ks

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Delta</th>
<th>Psi</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>285.56</td>
<td>43.33</td>
<td>95.4</td>
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<td></td>
<td>282.64</td>
<td>40.88</td>
<td>98.6</td>
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<td></td>
<td>285.44</td>
<td>43.88</td>
<td>95.1</td>
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<tr>
<td>2</td>
<td>277.08</td>
<td>36.72</td>
<td>105.0</td>
</tr>
<tr>
<td></td>
<td>277.84</td>
<td>37.08</td>
<td>104.3</td>
</tr>
<tr>
<td></td>
<td>280.4</td>
<td>38.96</td>
<td>101.3</td>
</tr>
<tr>
<td>3</td>
<td>283.92</td>
<td>43.52</td>
<td>95.7</td>
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<td>283.00</td>
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</tr>
<tr>
<td></td>
<td>277.12</td>
<td>36.60</td>
<td>105.1</td>
</tr>
</tbody>
</table>

Average ZrO₂ film thickness = 100.6 nm