STUDIES ON MICRO AND NANOTRIBOLOGICAL BEHAVIOUR OF Ti ALLOYS AND POLYMER

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Trends in Nanotribology
ICTP,Trieste,Italy
VIT University, Vellore India
My presentation will encompass

• Introduction to tribology of prosthesis
• Macro and nanotribology - Current scenario
• Experimental
  ➢ Scratch resistance of Ti and its alloys – from microscopic perspective
  ➢ Nanotribological behavior of Ti and its alloys
• Conclusions
Need to understand the tribology of prosthesis

Life span of the prosthesis 12-15 years

Expected life span – more than 30 years

**Reasons for short life span**
- infections
- corrosion
- wear
- lack of complete biocompatibility
- mismatch in modulus of elasticity
- manufacturing defects and surgical procedures

800,000 implants every year in Europe

By 2050, there will be approximately **2 billion elderly people** living worldwide.
Tribological contacts in hip joints

Materials

**Polymer** –
- UHMWPE

**Ceramics** –
- Alumina, Zirconia, TiN coatings on metallic materials

**Metals and alloys** –
- 316 Stainless steel
- Cobalt chrome
- Ti alloys
  - Ti6Al4V
  - Ti-6Al7Nb
  - Ti13Nb-13Zr
  - Ti-XTa-XNb-XZr-O

Sliding wear

Fretting wear

Metallic/ceramic ball

Metal/ceramic ball

Wear between Metal-bone Ball and stem, cup and ball
Ceramic over ceramic –

- installation problem
- Chip formation
- Revision if slight deviation in installation
- Fracture on high impact

excess of 1 million nanoparticles of with metallic implants are generated per step
Ti based biomaterials, the ultimate choice for orthopaedic implants – A review

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\textbf{ABSTRACT}

The field of biomaterials has become a vital area, as these materials can enhance the quality and longevity of human life and the science and technology associated with this field has now led to multi-million dollar business. The paper focuses its attention mainly on titanium-based alloys, even though there exists biomaterials made up of ceramics, polymers and composite materials. The paper discusses the biomechanical compatibility of many metallic materials and it brings out the overall superiority of Ti based alloys, even though it is costlier. As it is well known that a good biomaterial should possess the fundamental properties such as better mechanical and biological compatibility and enhanced wear and corrosion resistance in biological environment, the paper discusses the influence of alloy chemistry, thermomechanical processing and surface condition on these properties. In addition, this paper also discusses in detail the various surface modification techniques to achieve superior biocompatibility, higher wear and corrosion resistance. Overall, an attempt has been made to bring out the current scenario of Ti based materials for biomedical applications.

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Understanding of Tribology of Ti alloys
– Macroscopic point of view

Ti and its alloys have...
• Low shear strength and low tensile strength- high friction coefficient –
• Low resistance to plastic shearing and low work hardening, and
• Low protection exerted by the surface oxide which may form as a consequence of the high flash temperature induced by frictional heating
• High material transfer due to adhesive wear
• Strong tendency to seize
Nanotribology from a biomaterials perspective

• Understanding the polymer wear using AFM tip – Modeling AFM tip as an single asperity of counter metallic part

• Effect of surface roughness of polymer on wear at different hierarchical levels using microtribometer /AFM

• Nanotribological behavior of Ti and its alloys using -nanotribometer
Experimental Work

Phase 1
- Scratch testing -
- CONST./Ramp loading
- Cp Ti, Ti13Nb13Zr, Ti-6Al-4V, UHMWPE

Phase II
- Nanotribological studies
- Cp Ti, Ti13Nb13Zr, Ti-6Al-4V

Experimental conditions
- 3 Sliding speeds
- Dry dry/Simulated body conditions

9/27/2011
Scratch testing

- Rockwell indenter --C scale
- Angle (120. Cone)
- Tip radius 200µm

Outcome: Traction force, coefficient of friction, critical loads for failure (if coatings are characterized)
Scratch Hardness

• The scratch hardness is calculated by using the following formula,

\[ H_s = \frac{8 \times F_n}{\Pi \times b^2} \quad \text{(in GPa)} \]

where,

- \( H_s \) = scratch hardness,
- \( F_n \) = normal load applied,
- \( b \) = scratch width.
Microstructure, Roughness and Hardness

(i) Cp Ti-100x
(ii) Ti-6Al-4V 100x
(iii) Ti-13Nb-13Zr -100x

cpTi
Young's Modulus (100 GPa)
Poisson’s Ratio (0.36)

Ti6Al4V
Elastic modulus (112 GPa)
Poisson’s Ratio (0.342)

Ti13Nb13Zr
Young's Modulus (77 GPa)
Poisson’s Ratio (0.36)

E of the surface measured using SFM
Roughness of all the samples
## Constant Load Test

<table>
<thead>
<tr>
<th>Material</th>
<th>Start Load (N)</th>
<th>Stroke Length (mm)</th>
<th>Speed (mm/sec)</th>
<th>Offset (mm)</th>
<th>Traction Force</th>
<th>Scratch Width (in µm)</th>
<th>Scratch Hardness (in GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp-Ti</td>
<td>20</td>
<td>10</td>
<td>0.50</td>
<td>0.25</td>
<td>15.81</td>
<td>116.41</td>
<td>3.76</td>
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<td>0.25</td>
<td>45.86</td>
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<td>0.25</td>
<td>85.47</td>
<td>216.7</td>
<td>5.43</td>
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<td>Ti-13Nb-13Zr</td>
<td>20</td>
<td>5</td>
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<td>0.50</td>
<td>12.94</td>
<td>86.88</td>
<td>6.75</td>
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<td>Ti-13Nb-13Zr</td>
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<td>5</td>
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<td>0.50</td>
<td>35.72</td>
<td>109.90</td>
<td>10.55</td>
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<td>5</td>
<td>1</td>
<td>0.50</td>
<td>54.33</td>
<td>168.78</td>
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<td>97.08</td>
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<td>0.50</td>
<td>0.50</td>
<td>99.89</td>
<td>186.65</td>
<td>7.31</td>
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</tbody>
</table>
COF Comparison for CL

CL 20N

CL 50N

CL 100N
Constant Load Micro Scratch

Formation of Shear Planes
Severe Plastic Deformation
Plastic Deformation
Smooth Edges

CP Ti

TAV

Ti-6Al-4V
Traction Force Graph of Ti13Nb13Zr RL 20N
Traction Force Graph of C.P-Ti RL 50N
# Progressive Load Test

<table>
<thead>
<tr>
<th>Material</th>
<th>Start Load (N)</th>
<th>Stroke Length (mm)</th>
<th>Load Rate (mm/sec)</th>
<th>Speed (mm/sec)</th>
<th>Offset (mm)</th>
<th>Traction Force (N)</th>
<th>Scratch Width (in µm)</th>
<th>Scratch Hardness (in GPa)</th>
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<tbody>
<tr>
<td>Cp-Ti</td>
<td>20N</td>
<td>10</td>
<td>2N/mm</td>
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<td>0.25</td>
<td>28.82</td>
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<td>Cp-Ti</td>
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<td>10</td>
<td>2N/mm</td>
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<td>0.25</td>
<td>48.58</td>
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<td>Cp-Ti</td>
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<td>2N/mm</td>
<td>0.50</td>
<td>0.25</td>
<td>81.55</td>
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<td>Ti-13Nb-13Zr</td>
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<td>2N/mm</td>
<td>0.50</td>
<td>0.50</td>
<td>14.78</td>
<td>115.04</td>
<td>3.85</td>
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<td>Ti-13Nb-13Zr</td>
<td>50N</td>
<td>10</td>
<td>2N/mm</td>
<td>0.50</td>
<td>0.50</td>
<td>29.5</td>
<td>132.67</td>
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<td>10</td>
<td>5N/mm</td>
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<td>0.50</td>
<td>65.04</td>
<td>157.92</td>
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<tr>
<td>Ti-6Al-4V</td>
<td>20N</td>
<td>10</td>
<td>2N/mm</td>
<td>0.50</td>
<td>0.50</td>
<td>13.94</td>
<td>104.81</td>
<td>4.64</td>
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<tr>
<td>Ti-6Al-4V</td>
<td>50N</td>
<td>10</td>
<td>2N/mm</td>
<td>0.50</td>
<td>0.50</td>
<td>35.19</td>
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<td>Ti-6Al-4V</td>
<td>100N</td>
<td>10</td>
<td>5N/mm</td>
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<td>0.50</td>
<td>79.69</td>
<td>198.28</td>
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<td>Ti-6Al-4V</td>
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<td>5N/mm</td>
<td>0.50</td>
<td>0.50</td>
<td>80.69</td>
<td>217.70</td>
<td>8.06</td>
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Progressive Load Micro Scratch

**CP Ti**
- **Accumulation of Shear planes**
- **Formation of slip bands**
- **Chipped particles**

**TAV**
- **Cracking**

**Ti13.5**
- **Smooth Edges**
COF Comparison for RL

RL 20N

RL 50N

RL 100N
Scratch Testing of UHMWPE

CL 20N

CL 50N

RL 20N

RL 100N
## Scratch Hardness of UHMWPE

<table>
<thead>
<tr>
<th>Type of Load</th>
<th>Start Load (N)</th>
<th>Stroke Length (mm)</th>
<th>Load Rate (mm/sec)</th>
<th>Speed (mm/sec)</th>
<th>Offset (mm)</th>
<th>Traction Force</th>
<th>Scratch Width (in µm)</th>
<th>Scratch Hardness (in GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE CL</td>
<td>20N</td>
<td>10</td>
<td>2N/mm</td>
<td>0.50</td>
<td>0.25</td>
<td>14.3N</td>
<td>754</td>
<td>0.089</td>
</tr>
<tr>
<td>UHMWPE CL</td>
<td>50N</td>
<td>10</td>
<td>2N/mm</td>
<td>0.50</td>
<td>0.25</td>
<td>29.5N</td>
<td>1170</td>
<td>0.093</td>
</tr>
<tr>
<td>UHMWPE RL</td>
<td>20N</td>
<td>10</td>
<td>5N/mm</td>
<td>0.50</td>
<td>0.25</td>
<td>15.7N</td>
<td>907</td>
<td>0.062</td>
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<tr>
<td>UHMWPE RL</td>
<td>100N</td>
<td>10</td>
<td>5N/mm</td>
<td>0.50</td>
<td>0.25</td>
<td>55N</td>
<td>823.5</td>
<td>0.376</td>
</tr>
</tbody>
</table>
Nanotribology using CSM Nanotribometer

a) \( F_N \)  
\[
\text{Flat sample}
\]
\[
\text{Reciprocating sliding cycle}
\]

Ti alloy contact with alumina ball

b) Linear reciprocating module
Test conditions

- **Substrate:** CP Ti, Ti6Al4V, Ti13Nb13Zr
- **Ball:** Al₂O₃ (Alumina)
- **Ball diameter:** 1.5mm
- **No. of cycles/distance:** 30000 cycles/1mm stroke length
- **Acquisition Rate:** 20Hz
- **Speed:** 15, 20 and 25mm/s
  (characteristic for hip joints 0–50 mm/s- Gispert M.P. (2006))
- **Load:** 1.00N, contact stress - 154.9 MPa
- **Environment:** Dry and Ringer’s Solution
  - Ringer’s solution (g per 1 liter of water): NaCl 8.6; KCl 0.30; CaCl₂ 0.33; Na⁺ 147.00 mmol; K⁺ 4.00 mmol; Ca⁺ 2.25 mmol; Cl⁻ 155.60 mmol.
- **Air Temperature:** 25°C
Output

- Penetration depth
- Wear volume (ASTM G133 – 02)
- Coefficient of friction
DRY

15mm/s

COF | Penetration Depth | Wear Length | Wear Width
---|------------------|-------------|-------------
0.859 | 58.66μm | 0.689mm | 0.289mm

20mm/s

COF | Penetration Depth | Wear Length | Wear Width
---|------------------|-------------|-------------
0.688 | - | 0.723mm | 0.332mm

25mm/s

COF | Penetration Depth | Wear Length | Wear Width
---|------------------|-------------|-------------
0.583 | 47.6μm | 0.762mm | 0.272mm

CP Ti

Pulling due to adhesion

TAV

Longitudinal grooves

Ti13

Loose wear debris
RINGER’S SOL’N

**CP Ti**

**TAV**

**Ti13**

Tribo oxidation and tribo chemical wear

Elliptical wear scars
## COF Comparison

<table>
<thead>
<tr>
<th>Material</th>
<th>Dry</th>
<th>Ringer's Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15mm/s</td>
<td>20mm/s</td>
</tr>
<tr>
<td>CP Ti</td>
<td>0.859</td>
<td>0.688</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>0.725</td>
<td>0.728</td>
</tr>
<tr>
<td>Ti13Nb13Zr</td>
<td>0.802</td>
<td>0.789</td>
</tr>
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</table>
## Wear Volume Comparison

<table>
<thead>
<tr>
<th>Material</th>
<th>Sliding Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td>15mm/s 20mm/s 25mm/s</td>
</tr>
<tr>
<td>CP Ti</td>
<td>11.681 9.866</td>
</tr>
</tbody>
</table>

Note: Values are in $\text{mm}^3 \times 10^{-3}$.
Dry

Third body act as protecting layer and reduces friction

Ringer
SEM Images of worn track 15mm/s

Ti6Al4V-Dry

Ti13Nb13Zr-Dry

Ti6Al4V-Ringer’s

Ti13Nb13Zr-Ringer’s
SEM Images of worn track 25mm/s

- Ti6Al4V-Dry
- Ti13Nb13Zr-Dry
- Ti6Al4V-Ringer’s
- Ti13Nb13Zr-Ringer’s

Ti1313 exhibit rather smaller grains as a wear debris
TAV wear debris was larger
Ti6Al4V Dry EDS
TI6Al4V Ringer’s EDS
Scratch test

• The SEM images show that below the critical loads all samples were damaged by plowing, associated with the plastic flow of material
• Ploughing scratch, Pileup and debris were found on the sides
• In Ti-6Al-4V there were fine debris and large flakes, debris were strain hardened and also flakes abrade the surface and high COF results
• Level of deformation of Ti1313 compared to TAV should be up to 60% higher and exhibits high scratch hardness
Observations

• In TAV- With high sliding speeds, strain hardening is more and hardness increases in ductile material and low wear will occur

• At high speed, large dislocations and twinning occurs, dissipates large amt of energy producing sliding friction and resist the formation of cracks
Observations

• For TAV abrasive and adhesive operate at lower speed, due to accumulation of plastic strain which grows in size, cracks nucleate parallel to the surface and flakes are produced and results in cracking by adhesion and results in materials transfer.

• TAV plastic deformation along with strain hardening occurs and increases the surface hardness at high speed.

• Increase in wear resistance with increase in sliding speed.
Observations

• Ti1313 smearing and delamination
• Wear loss high at high speeds
• The penetration depth depend upon the hardness of the abrasives
• Adhesion is high in 1313 due to ductility and adhesion overlaps abrasion
• In case of 1313 thermal softening occurred and hardness decreased and wear progressed
• COF - smaller grains promote conformal area of contact thus reducing COF values
• The decrease of the grain size happened with speed increase resulting in decrease of COF and increase of wear volume
Observations

• In 1313 the hardness on the surface decreases due to thermal softening and this reduces YS and facilitating delamination.

• The alloys’ ability to recover their passive state during sliding depends mainly on the mechanical properties of the passive films and the contact pressure. On one hand the mechanical properties of the passive film depend mainly on the composition of the alloy.
Conclusions

• TAV exhibited more tribooxidation wear than Ti1313 = more black areas throughout the worn track.
• Ti1313 deforms the most under the same normal load, followed by CpTi and then TAV
• smaller particulate size is easier to remove from the wear surface with both abrasive and adhesive wear
• TAV and Ti1313 seems to have similar (abrasive, adhesive, tribochemical wear) but with difference of particulate grain size, especially in Ringer because TAV surface in Ringer is rather smooth, while Ti1313 has this grain surface structure even in Ringer (with smaller grain size in Ringer than at dry sliding)
• Ti1313 is more flexible (less stiff/rigid) than other 2 alloys