Implant Testing and Failure Analysis

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Overview

Introduction to titanium implants

7 questions related to implant testing and failure analysis:

1. What are the special features of titanium for implants?
2. Where does the coloration / discoloration of titanium implants come from?
3. Can titanium cause allergic reactions?
4. Do titanium implants corrode?
5. Is it allowed to combine titanium implants with other metals?
6. How can titanium implants break?
7. How notch sensitive is titanium?

Titanium: Application as bone implants

- Bone plates and screws
- Cups / backings
- Coatings
- Contourable implants

Titanium Alloys: Application as bone implants

- IM nails
- Pre-shaped bone plates
- Screws
- Spinal implants
- Non-cemented hip stems

Titanium: History

- 1795: Existence of Titanium suspected because of periodic table of the elements
- 1825: Titanium was detected
- 1925: Reduction to the pure titanium metal
- 1946: Industrial production of titanium
- 1965: AO ASIF introduced DC Plates in Titanium
- Today: Titanium is widely used in chemical industry, in aerospace and medicine

Implant Testing

- Chemical composition: Main elements*, trace elements*
- Microstructure*
- Hardness
- Static mechanical tests: Tensile*, bend test*, torsional test
- Surface properties: Roughness
- Fatigue
- Wear
- Corrosion
- Biocompatibility
- Cleanliness

* Requirements in ISO 5832 Standard
**Commerical Pure Titanium ISO 5832-2**

- α (T < 882°C) hexagonal close packed
- β (882°C < T < 1670°C) body centered cubic
- Fine-grained, single phase structure
- Grain size shall not be coarser than no. 5 according to ASTM E112

**TiCP – Chemical Composition**

CP titanium is classified into different Grades according to the level of impurities (Fe and O). The different Grades also have different strength levels.

<table>
<thead>
<tr>
<th>Grade</th>
<th>N (max.)</th>
<th>C (max.)</th>
<th>H (max.)</th>
<th>Fe (max.)</th>
<th>O (max.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 1</td>
<td>0.03</td>
<td>0.01</td>
<td>0.0125</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>Grade 2</td>
<td>0.03</td>
<td>0.01</td>
<td>0.0125</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>Grade 3</td>
<td>0.05</td>
<td>0.01</td>
<td>0.0125</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>Grade 4</td>
<td>0.05</td>
<td>0.10</td>
<td>0.0125</td>
<td>0.30</td>
<td>0.45</td>
</tr>
</tbody>
</table>

According to ISO 5832-2

**Combustion analysis of O, N, H, and C/S**

- **Oxygen:** Melting at up to 2700°C under He (inert carrier gas)
  - Reduction to CO
  - IR-detection
- **Hydrogen:** Melting at up to 2100°C under N₂ (inert carrier gas)
  - Detection of the change in the thermal conductivity
- **Nitrogen:** Melting at up to 2700°C under He (inert carrier gas)
  - Detection of the change in the thermal conductivity
- **Carbon and Sulfur:** Melting at up to 1300°C in reactive gas (oxygen, class 44)
  - Detection of CO₂ and SO₂ by selective IR-detection

**Combustion analysis of O, N, and H**

- Oxygen, nitrogen and hydrogen in solids, such as steel, non-ferrous metals, aluminium, titanium, zirconium, P/M materials, ores, ceramics, glass etc.

<table>
<thead>
<tr>
<th>Range of measurement:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen: 0.1 to 250 µg/g (ppm) to 200 µg/g (ppm) to 0.5% (2 ranges)</td>
</tr>
<tr>
<td>Nitrogen: 0.1 µg/g (ppm) to 0.5%</td>
</tr>
<tr>
<td>Hydrogen: 0.01 to 1000 µg/g (ppm)</td>
</tr>
</tbody>
</table>

  - Limit of detection: O, N, H 0.01 µg/g
  - O, N, H calibration: With standard specimens, certified reference materials or the integrated gas calibration unit using a reference gas

**O and N in CP Titanium**

Influence of oxygen (solid lines) and nitrogen (dashed lines) on the mechanical properties of titanium at ambient temperature [Zwickel]
Cold Deformation of CP Titanium

Influence of cold deformation by drawing on the mechanical properties of CP titanium [Zwicker]

Ti6Al-7Nb alloy
ISO 5832-11

25 µm

TiCP – Mechanical Properties

<table>
<thead>
<tr>
<th>Grade</th>
<th>Condition</th>
<th>Yield strength</th>
<th>Tensile strength</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AN</td>
<td>170 MPa</td>
<td>240 MPa</td>
<td>24%</td>
</tr>
<tr>
<td>2</td>
<td>AN</td>
<td>275 MPa</td>
<td>345 MPa</td>
<td>20%</td>
</tr>
<tr>
<td>3</td>
<td>AN</td>
<td>380 MPa</td>
<td>450 MPa</td>
<td>18%</td>
</tr>
<tr>
<td>4A</td>
<td>AN</td>
<td>483 MPa</td>
<td>550 MPa</td>
<td>15%</td>
</tr>
<tr>
<td>4B</td>
<td>CD</td>
<td>520 MPa</td>
<td>680 MPa</td>
<td>10%</td>
</tr>
</tbody>
</table>

Condition: AN = Annealed; CD = Cold Deformed

α and β-stabilizing Elements

Advantages
- Very good biocompatibility
- Good bone ingrowth (non-cemented systems)
- High corrosion-resistance (passive film)
- Low stiffness (stress shielding)
- Low density
- MRI compatibility
- Suitable as coating material

Disadvantages
- Limited mechanical strength
- Not very good for articulations depending from design and surface roughness, not suitable for cemented systems
- Relatively expensive
- Good bone ingrowth
- Bending properties
- Stainless steel is often sufficient

Microstructure: ETTC-2 / ISO 20160 Standards

Titanium as implant material

Implants for surgery - Metallic materials - Classification of microstructures for alpha-beta titanium alloy bars

Microstructure: ETTC-2 / ISO 20160 Standards

Meaning of the microstructure of TiAl and TiNi consists of a mixture of α- and β-grains.

The microstructure shall meet ratings A1 to A9

α-stabilizing elements: Al, O, N, C
β-stabilizing elements: Mn, V, Nb, W

c) in Ti nearly unalloyed Elements: Cu, Mn, Cr, Fe, Ni
Neutral Elements: Zr, Sn, …

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Bony Integration of Ti Implants

Integration can be an advantage or a disadvantage (implant removal)

Advantage: Tailored Surface

Different surface roughness according to application

- Sand blasted and acid etched
- Rough alumina blasted
- Etched + anodized
- Polished + anodized

Advantage: MRI Compatibility

Ti implants cause clearly less artifacts during magnetic resonance imaging compared to stainless steel

Advantage: Tailored Surface

CP Titanium: Coating Applications

Plasma Spray (Div.)
**CP Titanium: Coating Applications**

- **Plasma Spray**
  - Beads (Cups, knees, shoulders, ...)

- **Powder (RMG)**
  - Sintered porous structures (Div.)
  - Wires, mesh (Cups, stems)

**Titanium: Coating Applications**

- **Electrochemical treatment**
  - Modified chemical composition
  - Modified topography

- **Surface treatment by means of APC (SEM image)**
  - Uncoated
  - APC coated
  - Cage for spinal surgery (Patent EP 1372749)

- **PVD (Finger, Physiologic Hip)**
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Anodic Oxidation: Color Coding

- No painting, no coating
- Electrochemical growth of oxide layer to a defined thickness = „anodizing“
- 6 different colors possible
- Cleaning, washing, sterilization, contamination can modify color

Example: Discoloration of a midface plate

Discoloration of anodized midface
H-Plates during sterilization (steam/autoclave)
- Gold may turn to red
- Red may turn to gold

Possible reasons:
- Change in oxide layer thickness?
- Contamination of the surface?
XPS: Sputtering and Data Acquisition

Sputtering with Argon-Ions

XPS-Analysis of the sputtered surface

X-ray irradiation

Analysis Detector

Chemical information from „inside“ the specimen for

• Reference measurement (bulk material)
• Depth profile (Oxide layer, Coatings, Carburization, ...)

XPS survey spectrum

Survey spectrum H plate

Intensity [Cps]

Binding energy [eV]

XPS sputtering

Depth profile of the golden anodisation:

• Layer composition
• Layer thickness

Layer thickness gold: ca. 110 nm (Sputterrate: 5 nm/min)
Layer thickness red: ca. 120 nm

Summary

• No relevant contamination, foreign elements not responsible for discoloration
• Aluminium and silicon dioxide particles on the surface, but not responsible for discoloration
• Minor changes in the oxide layer thickness cause the colour shift from gold to red
• Minor oxidation or layer abrasion can lead to discolorations

Corrective actions:

• Choose a slightly lower voltage for gold anodization and a slightly higher voltage for red anodization

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Titanium Allergies?

Nickel, chromium, and cobalt are known allergenes. Titanium is mostly judged as non-critical, but:


![Graph showing in vitro lymphocyte reaction to titanium](image)

Metal Allergies Related to Implants

- Other possible influences
  - Wear debris from instruments: Drill bits, Sleeves (hardened steel)
  - Drugs
  - Impurities / residues from implant production (blasting media, copper)
- Explants should be available for investigation
  - Check for chemical composition
  - Check for cleanliness

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Do titanium implants corrode?

![Image of corrosion on titanium](image)

Corrosion of Surgical Instruments

- Corrosion resistance
  - Titanium is very reactive...
    - In the presence of oxygen (in water, air and physiologic solutions) the surface reacts...
  - A stable, dense, about 3 nm thin oxide layer is formed (passive layer)
    - This titanium oxide layer is responsible for the outstanding corrosion resistance of titanium in physiologic solutions
    - What happens if this layer is destroyed locally (e.g. by scratching with a surgical instrument)?
  - No negative effect, because the layer is rebuilt spontaneously and immediately
Methods: Electrochemistry by EC-Pen

Example for pitting corrosion

Corrosive breakthrough of the passive layer (pitting)

Example for crevice corrosion

Broken 11.0 mm Femoral nail, Implant Steel ISO 5832-1 with traces of corrosion

Pitting Corrosion

Ti-6Al-7Nb alloy: Potentiodynamic testing

- Definition Pitting Corrosion:
  Localized corrosion of a metal surface at, or immediately adjacent to an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.

- Crevices are critical because of...
  - Local differences in O₂ concentration (repassivation ability)
  - Local differences in pH (Hydrolysis → pH decrease)
  - Local differences in Cl⁻ concentration

Crevice Corrosion

• Definition Crevice Corrosion:

- Localized corrosion of a metal surface at, or immediately adjacent to an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.

• Crevices are critical because of...

- Local differences in O₂ concentration (repassivation ability)
- Local differences in pH (Hydrolysis → pH decrease)
- Local differences in Cl⁻ concentration

Crevice Corrosion: Stainless Steel

Crevice Corrosion: Titanium Implants (TiCP)
Conclusions Crevice Corrosion

- Most common corrosion phenomena in implants
- Often found on the fatigue fracture surfaces of broken Stainless Steel implants, less often on broken titanium implants
- Modular systems (multi component) with crevices are critical
- Combination with laser marking in the crevice should be avoided

Material combinations in implant systems

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Studies on Galvanic Corrosion of Implants

- In vitro Studies (Corrosion Tests)
- In vivo Studies (Case Studies)
- Large prospective / retrospective Studies

- Generally accepted: All combinations of Co-base and Ti-base implant alloys
- Debated: All combinations of implant Stainless Steel with Co-base and Ti-base alloys

Galvanic Corrosion: Definitions

- Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially when in electrical contact with a different type of metal and both metals are immersed in an electrolyte
- Corrosion associated with the current of a galvanic cell consisting of two dissimilar conductors in an electrolyte
- Difference in electrochemical potential
- Surface area ratio
- Passive layer


- Most of the articles arguing against the mixing of dissimilar alloys in implant systems rely on just one in vitro study by Griffin et al.
- Surprisingly, this publication comes to the conclusion that mixing of 316L implant steel to Co- or Ti-based alloys is not recommended, although the stainless steel alone showed approximately the same corrosion resistance as the different combinations of materials.

- Most important study on the question of mixing SS and Ti
- Theoretical work on the mixing
- Sheep study on the tissue compatibility
- Clinical study with more than 500 patients
- Conclusions: combination of SS and Ti react like the “less noble” partner of the two (stainless steel)
- It should be permitted to combine an elastic titanium plate with stronger stainless steel screws
- Combination of Ti plates with SS screws did not show any clinical or radiographic disadvantages in more than 500 patients.

Mixing of Metals is practiced...

- Information from clinics and surgeons: Stainless Steel and Ti implants are mixed in some cases
- Adverse effects are not known from literature
- Mixing is not often performed in European and northern American countries but more frequently in countries of southern America, Africa or Asia where stock logistics are sometimes more problematic


- Study of 139 explanted modular femoral hip protheses
- Co-alloy femoral head + Ti-alloy stem results in the potential for galvanically-accelerated crevice corrosion
- Corrosions only observed in the mixed metal protheses (25 out of 48 cases) not in single-alloy, modular components, even after longer implantation.
- No specimens corroded after less than nine months in vivo, but all with more than 40 months
- Study clearly shows increased crevice problems in the routinely performed combination of CoCr-alloys and Ti-alloys.

Mixing of Metals is practiced...

- Specific case of mixing of Ti-alloy and SS screws in the same Ti-alloy bone plate operated in Austria was reported to the RMS Foundation
- Retrieval after few weeks of implantation following an implant failure not related to the mixing of materials
- Stainless steel screws showed some staining but no extensive corrosion signs. The surgical report did not mention the fact of mixing of materials.


... but not allowed

- All major orthopaedic implant manufacturer (DePuy, Biomet, Zimmer, Stryker, Smith & Nephew, Synthes) advice not to combine Ti and SS in situations of direct contact in implant systems

DePuy (Johnson & Johnson):

WARNINGS
MIXING METALS CAN CAUSE CORROSION. There are many forms of corrosion damage and almost all of these occur on metals surgically implanted in humans. General or uniform corrosion is present on all implanted metals and alloys. The rate of corrosive attack on metal implant devices is usually very low due to the presence of passive surface films. Dissimilar metals in contact, such as titanium and stainless steel, accelerate the corrosion process of stainless steel and more rapid attack occurs. The presence of corrosion often accelerates fatigue fracture of implants. The amount of metal compounds released into the body system will also increase. Internal fixation devices, such as rods, hooks, wires, etc., which come into contact with other metal objects, must be made from like or compatible metals. Avoid coupling of stainless steel with the Surgical Titanium Mesh System implants.
Standard EN ISO 21534:2009

- Non-active surgical implants - Joint replacement implants - Particular requirements (ISO 21534:2007) Appendix C (Informative)

- Suitable combinations of dissimilar metals without articulation:
  - Co-base alloys + Ti alloys (TAN, TAV)
  - Dissimilar Co-base alloys
  - Implant Stainless Steel + Ti alloys (TAN, TAV)
  - Dissimilar Implant Stainless Steels
  - SS ISO 5832-9 + Co-base alloys

- Unsuitable combinations of dissimilar metals without articulation:
  - Stainless Steel ISO 5832-1 + Co-base alloys
  - Stainless Steel ISO 5832-1 + CP Ti

Conclusions Galvanic Corrosion

Based on this information it can be concluded that:

- Some facts indicate that today’s quality implant materials like implant stainless steel, Co-alloys, and Ti-alloys can safely be combined in stable implant systems
- The passive surface protective layer is thought to be sufficient to prevent excessive galvanic currents in non-critical situations
- Combinations will not be worse than the less noble partner in many combinations
- More severe conditions (crevice, fretting or pitting) may destroy the protective layer resulting in dissolution of the metal components accelerated by the galvanic potential difference. This is confirmed by a large study on explanted modular hip components
- When mixing SS with Ti- or Co-Alloys, it may be recommended to choose a stainless steel of higher corrosion resistance (ISO 5832-9 or better) and to absolutely avoid fretting and crevice situations (difficult in modular systems)

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Product Failure

- Patient (female), 39 y, 64 kg, Ulna shaft fracture left

Bone fracture 16.09.2003
Op 17.09.2003
Plate fracture 19.12.2003

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Investigation of Plate Failure

- Non-cemented hip stem, Ti6Al7Nb alloy with hydroxyapatite coating
- HFR Hôpital Cantonal Fribourg
- Failure of the hip stem in the neck, around 13 mm below the cone
- Anamnesis
  - Male patient, born 1941
  - Initial implantation 20.10.2009
  - Revision: 20.01.2011, Exchange of femoral head (instability)
  - Date of prosthesis fracture: unknown
  - Explantation: 22.10.2012

Titanium and Notch Sensitivity
Titanium and Notch Sensitivity

Overview: Received parts

Detail: Fracture site

Titanium and Notch Sensitivity

Investigations
- Macroscopic documentation
- Examination of the raw material certificates
- Examination of fracture surface (SEM) and material identification (EDX)
- Metallography
  - Microstructure: Transversal and longitudinal
  - Vickers hardness

Titanium and Notch Sensitivity

Distal fracture surface with rounded edges

Titanium and Notch Sensitivity

Overview of the proximal fracture surface (sputtered). Less damaged but still rounded edges

Titanium and Notch Sensitivity

Fatigue striations

Mixed fracture

Forced fracture
Titanium and Notch Sensitivity

EDX: Identification as TiAlNb alloy

Transversal cut: Alpha/Beta-Microstructure A4 according to ISO 20160


The End

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Your questions?

Titanium and Notch Sensitivity

- Raw material certificate according to ISO 5832-11
- Numerous surface destruction sites visible macroscopically
- Fracture surface analysis:
  - Fracture initiation not localised clearly (lateral)
  - Destruction of the surface not clearly identified
  - Fatigue fracture
  - Relatively large portion of forced fracture (50%)
- EDX confirms TiAlNb alloy
- Microstructure and hardness are according to the standard (315 HV - 914 MPa; ISO 5832-11: min. 900 MPa)
- No indication for a material or manufacturing defect
- Stress concentration due to surface destruction in the area of highest load provoked the formation of a crack
- Titanium is known to be highly notch sensitive