Annealed titania nanotubes: Wettability and corrosion behavior of modified Ti-6Al-4V

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Introduction

Osseointegration

Corrosion

Tribological

Mechanical
Surface Treatments:
Electrochemical Anodization

Anodic Polarization: 60V, 2h (ethylene glycol + 4vol% d.i. water + 0.2 wt.% NH₄F)

Compact oxide

Porous oxide

Self-ordered titania nanotubes

Ti-6Al-4V

F⁻O²⁻

[TiF₆]²⁻

Oxide Layer

Ti-6Al-4V

Ti-6Al-4V

Ti-6Al-4V
Surface Treatments: Thermal Oxidation

Two Effects

1. Growth of the compact oxide layer
2. Polycrystalline titanium dioxide (anatase/rutile)

(Garcia & Deskins 2012)
Objectives/hypothesis

1. Evaluate the hydrophilic behavior of treated titanium alloy substrates over 25 days
2. Evaluate the electrochemical impedance and corrosion/passivation behavior of treated titanium alloy substrates in cell culture medium at physiological temperature
3. Evaluate the osteoblast adhesion response to treated titanium alloy substrates
Experimental design

Surface Modifications (Ti-6Al-4V discs)

- Polished (Smooth)
- Thermally Oxidized (TO) 600°C, 3h
- Anodized (Ad) 60V, 2h
- Anodized 60V, 2h + Thermally Oxidized 600°C, 3h (Ad+TO)

Surface Characterizations
- Water Contact Angle Aging
- Fourier Transform Infrared Spectroscopy
- Field Emission Scanning Electron Microscopy
- Brunauer-Emmett-Teller Surface Area

Corrosion Tests
1. OCP (1h)
2. EIS (± 10 mV from OCP)
3. Potentiodynamic (-1V vs. SCE-1.8 V vs. SCE)
Results: WCA

<table>
<thead>
<tr>
<th>Time</th>
<th>Smooth</th>
<th>Annealed 600°C, 3h</th>
<th>Anodized 60V, 2h</th>
<th>Anodized 60V, 2h + Annealed 600°C, 3h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td><img src="Smooth_Day0.png" alt="Image" /></td>
<td><img src="Annealed_Day0.png" alt="Image" /></td>
<td><img src="Anodized_Day0.png" alt="Image" /></td>
<td><img src="Anodized_Annulled_Day0.png" alt="Image" /></td>
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<tr>
<td>Day 7</td>
<td><img src="Smooth_Day7.png" alt="Image" /></td>
<td><img src="Annealed_Day7.png" alt="Image" /></td>
<td><img src="Anodized_Day7.png" alt="Image" /></td>
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<tr>
<td>Day 14</td>
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<td><img src="Annealed_Day14.png" alt="Image" /></td>
<td><img src="Anodized_Day14.png" alt="Image" /></td>
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<tr>
<td>Day 25</td>
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<td><img src="Annealed_Day25.png" alt="Image" /></td>
<td><img src="Anodized_Day25.png" alt="Image" /></td>
<td><img src="Anodized_Annulled_Day25.png" alt="Image" /></td>
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</tbody>
</table>
Results: WCA

- WCA: Ad+TO<Ad<TO<Smooth
- Ad+TO showed increased wettability over 25 days of aging (p<0.001)
Results: FESEM, BET

- Used Krypton gas as adsorbate
- For anodized samples, SA = 0.33 m$^2$/g (correlation = 0.998)
- Based on mass of sample and exposed area to the electrolyte, corrosion SA ~ 300 cm$^2$
Results: Potentiodynamic

![Graph showing potentiodynamic plots for Smooth, TO, Ad, Ad+TO](image)

- **Smooth**
- **TO**
- **Ad**
- **Ad+TO**

![Micrographs of Ad and Ad+TO](images)

- **Ad**
- **Ad+TO**
Results: OCP, Potentiodynamic

**Open Circuit Potential**

- Potential (V vs. SCE)
- Log Current Density (μA/cm²)

**Ecorr**

- Potential (V vs. SCE)

**Icorr**

- Log Current Density (μA/cm²)

**Ipash**

- Log Current Density (μA/cm²)
Results: EIS Modeling
Results: EIS

Rp

Reff

CPEeff
Progresses: Cell Culture

- 36 discs total
- DMEM + 10% FBS + 1% antibiotic
- MC3T3-E1 Pre-Osteoblasts
- Cell attachment assay
Future work

• Optimize nanotube dimensions and annealing temperature/duration for corrosion resistance

• Optimize nanotube dimensions and annealing temperature/duration for osteogenic response: adhesion, proliferation, differentiation

• Understand the effect of spontaneous voltages on cellular viability with titania nanotubes