„CeraPore“ –
Structural surface modification of dense load-bearing ZTA

Norbert Schneider
Content

- Background
- Coating and sintering process
- Surface properties
- Mechanical properties
- Cellbiological / Clinical results
- Regulatory aspects
- General project risks
Background

- high wall thickness of the system
- risk of surgical error when seating ceramic insert
- risk of aseptic loosening due to metal ions
intelligent composite materials

nacre

bone

Damascene-steel

BIOLOX® delta

www.larimar.de

www.digitalefolien.de

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nacre

**composite-Werkstoff:**
- 95% aragonite
- 5% proteins & chitin

**Young’s modulus:**
- up to 80 GPa

**fracture toughness:**
- 1 - 8 MPa m$^{1/2}$
Bone

- **Composite material:**
  - 70% hydroxyapatite & calciumphosphate
  - 20% collagen & proteoglycane
  - 10% water

- **Young's modulus:**
  - Appr. 30 GPa

- **Fracture toughness:**
  - 2 – 12 MPa m$^{1/2}$
Damascene steel

- **Composite Material:**
  - 50% low-C steel
  - 50% rich-C- or P steel

- **Young’s Modulus:**
  - 210 GPa

- **Fracture Toughness:**
  - 50 MPa m$^{1/2}$
**BIOLOX® delta**

**composite-material:**
- 80% Al₂O₃
- 17% ZrO₂
- 3% toughening platelets

**Young’s modulus:**
- 360 GPa

**fracture toughness:**
- 6.5 MPa m¹/²
Transformation toughening of ZrO$_2$

tetragonal:  
$\rho = 6.10 \text{ g/cm}^3$

monoclinic:  
$\rho = 5.85 \text{ g/cm}^3$

1170 °C < T

increase of volume

4 %

T < 1170 °C
Toughening mechanisms in BIOLOX® delta
3-point-bending strength
Microstructure of BIOLOX® ceramics

**BIOLOX®forte**

- 99.8 Vol.% Al$_2$O$_3$ + 0.2 Vol.% other oxides

**BIOLOX®delta**

- 80 Vol.% Al$_2$O$_3$ + 17 Vol.% ZrO$_2$ + 3 Vol.% other oxides
### Material properties of BIOLOX®-ceramics

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>BIOLOX®forte Mean value</th>
<th>BIOLOX®delta Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ Vol.%</td>
<td>99,8</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>ZrO₂ Vol.%</td>
<td>n.a.</td>
<td></td>
<td>17</td>
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<tr>
<td>mean grain size µm</td>
<td>1,75</td>
<td></td>
<td>0,56</td>
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<tr>
<td>4-point-bending-strength MPa</td>
<td>631</td>
<td></td>
<td>1384</td>
</tr>
<tr>
<td>Young’s modulus GPa</td>
<td>407</td>
<td></td>
<td>358</td>
</tr>
<tr>
<td>frac. toughn. KᵢC MPa m¹/²</td>
<td>3,2</td>
<td></td>
<td>6,5</td>
</tr>
</tbody>
</table>
Aim of the project

- Development of a porous ceramic coating based on BIOLOX®delta for all-ceramic joint replacement

- Reduced wall thickness (3 mm) → lower outer diameter

- Improved functionality → combination of superior tribological properties of ceramics and direct osseointegration

- Monolithical system → simplified implantation, avoiding surgical errors
Content

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Coating process

spraying of ceramic slurry

green body

semi-automated process
Coating process

spraying of pore forming agent

- pore forming agent: organic material
- pore forming agent is completely removed during sintering process
thermical removing of pore forming agent

properties of coating depend on sintering temperature, pressure and sintering time
Surface treatment after sintering

- removing mechanically unstable parts of the coating
- pore opening

blasting process

finished coating surface

0.5 mm
Coating process is bench-scale unit
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Characterization: optical microscope / SEM

- surface porosity: app. 47%
- pore size (diameter): 200 – 500 µm
- hemispherical pores
- surface enlargement by factor 2 to 3

highly reproducible surface structure
Characterization: Laser-scanning-microscope

roughness: \( R_z = 435 \, \mu m \)
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- **Mechanical properties**
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Characterization: compression strength

Test machine limit = 19 kN

→ weight equivalent 1,9 t
→ steel bolts were deformed
→ no damage occurred at the coating
Characterization: shear strength

- **Shear strength**: 25 mm
- **Acceptance criterion of ASTM F1044-05**

- **No delamination of the coating**

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Characterization: adhesive strength

![Graph showing adhesive strength](image)

Characterization

- Steel bolt
- Substrate
- Coating (FM1000)

![Images of samples](image)

Teil 1  Teil 2  Teil 3  Teil 4  Teil 5

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Characterization: biaxial bending strength

- 36 %
- 31 %

Flexural strength [MPa]

n = 15
uncoated reference
coated samples with pore forming agent
coated samples without pore forming agent

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Analysis of fracture origin

Fracture origin

substrate
coating
pore
Requirements:

→ Testing geometry hip joint cup
→ bearing couple 40 mm diameter
→ wall thickness as small as possible

(minimized space requirement)

Cup-Design relates to:

→ range of motion
→ luxation stability
→ mechanical stability
→ production process
In-vivo like burst-test without backside support

Stress-analysis
(Finite Element Methode)

Burst-Test axial

Test Setup

Burst-Test 45°
according
„upright standing“
Acceptance criteria for regular ceramic inserts in metal shells:

- **Burst-test axial**
  - Mean value: 150 kN
  - Std. dev.: 40 kN
  - n = 7

- **Burst-test 45°**
  - Mean value: 118 kN
  - Std. dev.: 14 kN
  - n = 7
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- **Cellbiological / Animal study results**
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Osseointegration in biological study

Schreiner, Schulze, Schwarz et al., ZOrthopUnfall 2011

52 weeks after implantation
Osseointegration in biological study

Masson-Goldner stain

Schreiner, Schulze, Schwarz et al., ZOrthopUmfall 2011

near-rim area 1 near-rim area 1
area of pole 2

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Osseointegration in biological study

Schreiner, Schulze, Schwarz et al., ZOrthopUnfall 2011

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Cell-tests (humane osteoblasts) of different pore size distributions

<table>
<thead>
<tr>
<th>Pore size (diameter) [µm]</th>
<th>Proliferation after 24 h (n=14)</th>
<th>Proliferation after 96 h (n=14)</th>
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</thead>
<tbody>
<tr>
<td>750-660 A</td>
<td>57</td>
<td>103</td>
</tr>
<tr>
<td>660-590 B</td>
<td>54</td>
<td>127</td>
</tr>
<tr>
<td>590-350 C</td>
<td>34</td>
<td>141</td>
</tr>
<tr>
<td>350-200 D</td>
<td>64</td>
<td>134</td>
</tr>
<tr>
<td>no pores Ref</td>
<td>57</td>
<td>118</td>
</tr>
</tbody>
</table>

Cell culture on synthetics (reference) 96 h

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Test of osseointegration

+ Hydroxyapatite, \( \text{Ca}_5[\text{OH(PO}_4)_3] \)
  - inorganic part of bone
  - no development of connective tissue

+ Plasma-activation
  - decrease of contact angle (↓)
  - increase of surface energy (↑), leads to higher adhesion of bone cells
  - reaction gas: oxygen
  - durability: 4 days (reversible reaction)

+ RGD-Peptides
  - protein of extracellular matrix
  - adhesion of cells using Integrin-coupling
  - mechanically stable cell network

not activated

with O\(_2\)-Plasma activated

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Osseointegration in biological study (sheep)

8 mm

11 mm

4 implants per leg

Bulk material (pink)

Coating (pink)

Bone (green)

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Osseointegration in biological study (sheep)
Biological study – comp. to literature

Biological studies with Ti-samples

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>1.5</td>
<td>2.5</td>
<td>3.5</td>
<td>4.5</td>
<td>5.5</td>
<td>6.5</td>
<td>16</td>
</tr>
</tbody>
</table>

fatigue-test:
cementing on Sawbone® using Palacos®R,
1.5 million cycles, 5 Hz
with flexion angles of 8°, 15° and 110°
highest load 2.6 kN
lowest load 168 N
outer/inner rotation between -1.9° and +5.7°
Cement compatibility

Post-fatigue pull-off test:
way-controlled, 5 mm/min
Coating process is reproducible

Alumina-Zirconia-ceramics are biocompatible materials

Porous coating leads to bone ingrowth ⇒ shear strength of bone and implant is comparable with Titanium implants

Coating is fully bonded to substrate during sintering ⇒ very good mechanical testing results ⇒ acceptance criteria of FDA passed!
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