ANALYSIS OF SELECTIVE LASER MELTING OF RESORBABLE BIOCERAMICS

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OBJECTIVES OF THE PROJECT

WHAT COULD BE POSSIBLE IN A NEAR FUTURE...
OBJECTIVES OF THE PROJECT

DESIGN/MANUFACTURING OF BIOCERAMIC IMPLANT

- Better Osteointegration of the Implant (Compared to Metallic Implants)
- Implant as a Bone-repair-kit: Induction of Natural Bone Regeneration by the Implant

OrthoFlase Project

Projet ANR-11-TECS-0005:OrthoFlase

SMEs

Project leader

R&D partners

Web-based software and data management

Powder

Biocompatibility

Process development
OBJECTIVES OF THE PROJECT

STATE-OF-THE-ART/EXISTING TECHNOLOGY

- Scanning
- Data processing and CAD generation
- Othopedic Surgeon
- Debinding/Sintering
- 3D printing
- Surgery
- Sterilisation
- HAP (Hydroxyapatite)
- TCP Tricalcium Phosphate

Miguel Castilho & al., Biofabrication 5 (2013) 035012 (12pp)
OBJECTIVES OF THE PROJECT

R&D AND INNOVATIONS PROPOSED

Web-based CAD/CAM and MMI

Othopedic Surgeon

Data processing and CAD generation

Scanning

Growing factors, bone cells

Bio-active implant

Sterilisation

Direct Manufacturing

SLM of HAP or TCP

Surgery

+ Production of very pure TCP powder of SLM
  (very low content of metallic elements)
MANUFACTURING PROCESS OF TRICALCIUM PHOSPHATE B (B-TCP)

- Chemical synthesis of Apatitic Tricalcium Phosphate
- Conversion into TCP
- Synthesis of macro-powder by spraying

SYNTHESIS OF APATITIC TRICALCIUM PHOSPHATE (TCP AP)

Aqueous precipitation

\[
6 \text{(NH}_4\text{)}_2\text{HPO}_4 + 9 \text{Ca(NO}_3\text{)}_2 + 6 \text{NH}_4\text{OH} \rightarrow \text{Ca}_9(\text{PO}_4)_5(\text{HPO}_4)(\text{OH}) + 18 \text{NH}_4\text{NO}_3 + 5 \text{H}_2\text{O}
\]

\[
\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH}, n\text{H}_2\text{O} \rightarrow 3 \text{Ca}_3(\text{PO}_4)_2 + (n+1)\text{H}_2\text{O}
\]

**β-TCP**

- Ultra pure composition (TCP >99.5% wt., Metals <50ppm)
- Dense and spherical aggregates
- Size distribution: \(1 \leq \phi \leq 50 \mu\text{m}\)
Demonstrator Setup

SLM demonstrator system
- Laser : CW (100W), CO₂ (50W) (nanoseconde fiber laser, CW Nd:YAG, NIR diode : available)
- Manufacturing Chamber : Ø100mm, stainless steel with HAP

Process parameter search
- Instrumentation with high speed camera
- Fusion lines
- Main parameters : Power, Scanning speed, Layer thickness, Laser spot diameter,…
SLM PROCESS STUDY : POWDER ABSORBIVITY

ABSORBIVITY OF TCP POWDER : STATIC TEST

- 838 nm (Thalès laser diode) (spot ~1 mm)
  - No absorption at 50 W

- 1,064 µm (laser Nd:YAG 3 kW Lamp pumped) (spot diam ~1.5 mm)
  - No absorption up to 750 W

- 10.6 µm (CO2 laser 50 W max)
  - Fusion at few Watts

✔ Study with CO2 laser possible

✔ For NIR lasers (1,064 µm, 1.07 µm, 838 nm, ...) : need to modify the powder...
**Initial trials**

Powder thickness : 200µm  
Support : HAP coating

<table>
<thead>
<tr>
<th>Trial</th>
<th>Power</th>
<th>Speed</th>
<th>Foacal spot diam.</th>
<th>T° heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCP_CO2_C1_L4</td>
<td>52 W</td>
<td>0,1 m/s</td>
<td>6 m/min</td>
<td>200 µm</td>
</tr>
<tr>
<td>TCP_CO2_C1_L5</td>
<td>52 W</td>
<td>0,25 m/s</td>
<td>15 m/min</td>
<td>200 µm</td>
</tr>
<tr>
<td>TCP_CO2_C1_L6</td>
<td>52 W</td>
<td>0,25 m/s</td>
<td>15 m/min</td>
<td>200 µm</td>
</tr>
<tr>
<td>TCP_CO2_C1_L7</td>
<td>52 W</td>
<td>0,05 m/s</td>
<td>3 m/min</td>
<td>200 µm</td>
</tr>
</tbody>
</table>

**Results:**

- Fusion in droplets for highest speed
- No enough energy density to get stable fusionTCP
- Need to decrease speed
Reducing travel speed

<table>
<thead>
<tr>
<th>Trial</th>
<th>Power</th>
<th>Speed</th>
<th>Focal spot diam.</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCP_CO2_C1_L1</td>
<td>52 W</td>
<td>1 m/min</td>
<td>200 µm</td>
<td>~300µm</td>
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<tr>
<td>TCP_CO2_C1_L2</td>
<td>52 W</td>
<td>1.5 m/min</td>
<td>200 µm</td>
<td>~250µm</td>
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<td>TCP_CO2_C1_L3</td>
<td>52 W</td>
<td>2 m/min</td>
<td>200 µm</td>
<td>~200µm</td>
</tr>
</tbody>
</table>

Powder thickness: 200µm
Support: HAP coating

Results

- Generation of continuous and stable fusion of TCP
- Numerous cracks
- Further process parameter optimization

Heating of manufacturing chamber
Need to decrease powder thickness, increase travel speed and laser power...
SLM PROCESS STUDY: CW FIBER LASER

ADDITION OF PARTICLES TO TCP POWDER
- Biocompatibility
- Sub-micro, nano

\[ \text{TiC, SiO}_2, \text{ SiC} \ldots \]

B-TCP+nano SiC

First method
- Use of \( \beta \) TCP powder
- Mechanical mixing with nano-SiC powder

Second method
- Co-spray drying SiC - \( \beta \) TCP
  - Elaboration of dense and spherical aggregates
  - Particle size distribution: \( 1 \leq \phi \leq 50 \ \mu m \)
1. PARAMETER SEARCH FOR 2D LINE ON SUBSTRATE
   • HAP coating stainless steel plates
   • Power : 30-100W
   • Focal spot diameter: ~100µm
   • Scanning speed : 1-200mm/s
   • Selection of best fusion profile (stability)

2. PARAMETER SEARCH FOR 2D SURFACE
   • Power : 30-100W
   • Focal spot diameter: ~100µm
   • Scanning speed : 100-200mm/s
   • Distance between 2D line : 50%-100% of line width and grids
3. BUILDING 3D SIMPLE GEOMETRIES

- Squares, cylinders, ...
- Focal spot diameter: \( \sim 100\mu\text{m} \)
- Scanning speed: 1-200mm/s

<table>
<thead>
<tr>
<th>Sample</th>
<th>G1.2</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>200mm/s – ( Ec=0.5\text{mm} ) - carré</td>
<td><img src="carr%C3%A9_200mm" alt="Image" /></td>
<td><img src="carr%C3%A9_200mm" alt="Image" /></td>
</tr>
<tr>
<td>200mm/s – ( Ec=0.5\text{mm} ) - cylindre</td>
<td><img src="cylindre_200mm" alt="Image" /></td>
<td><img src="cylindre_200mm" alt="Image" /></td>
</tr>
<tr>
<td>200mm/s – ( Ec=0.5\text{mm} ) - triangle</td>
<td><img src="triangle_200mm" alt="Image" /></td>
<td><img src="triangle_200mm" alt="Image" /></td>
</tr>
<tr>
<td>220mm/s – ( Ec=0.5\text{mm} )</td>
<td><img src="220mm_200mm" alt="Image" /></td>
<td><img src="220mm_200mm" alt="Image" /></td>
</tr>
</tbody>
</table>
SLM PROCESS STUDY : CW FIBER LASER

MATERIAL ANALYSIS
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Detail of the microstructure

Rich Ca,O zone

Detail of structure

Pure β-TCP XRD spectrum

XRD spectrum
CONCLUSION AND PERSPECTIVES

Process parameter search

1. CO2 laser: Continuation of process parameter search for 3D part manufacturing
   - Decrease powder thickness
   - Increase of travel speed
   - Decrease of cracks
   - Manufacturing of 3D parts

2. Fiber laser

3. Material study

4. Manufacturing complex part

Biological tests

1. 3D samples

2. Study of porosity of the sample

New additional material

Optimization of mixture (TCP+add)

Composition

Fraction of B-TCP, HAP, TTCP,…