Survey of Materials
and Material Issues in
Rapid Manufacturing by SLS/SLM

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Prof. G. Levy, inspire, St-Gallen, Switzerland

Selective Laser Sintering/Melting: materials

- Polymer
- Metal (Steel)
- Ceramic (Al₂O₃)
- Composite (Cermet-HM)
- Metal (Ti)
**Classification of binding mechanisms**

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering
   - Partial Melting
3. Full Melting
4. Chemically Induced Binding

**Main binding mechanisms for polymers**

Polymers

<table>
<thead>
<tr>
<th>Binding mechanism classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Solid State Sintering</td>
</tr>
<tr>
<td>1.1 separate structural and binder particles</td>
</tr>
<tr>
<td>1.2 composite particles</td>
</tr>
<tr>
<td>1.3 coated grains particles</td>
</tr>
<tr>
<td>2. Liquid Phase Sintering</td>
</tr>
<tr>
<td>2.1 single phase material</td>
</tr>
<tr>
<td>2.1.1 partially molten</td>
</tr>
<tr>
<td>2.1.2 fusing powder mixture</td>
</tr>
<tr>
<td>2.2 double phase material</td>
</tr>
<tr>
<td>2.2.1 partially molten</td>
</tr>
<tr>
<td>2.2.2 fusing powder mixture</td>
</tr>
<tr>
<td>3. Full Melting</td>
</tr>
<tr>
<td>3.1 single component resin material</td>
</tr>
<tr>
<td>3.2 double component material</td>
</tr>
<tr>
<td>3.2.1 partially molten</td>
</tr>
<tr>
<td>3.2.2 fusing powder mixture</td>
</tr>
<tr>
<td>4. Chemically Induced Binding</td>
</tr>
<tr>
<td>4.1 double component resin material</td>
</tr>
<tr>
<td>4.2 double component material</td>
</tr>
<tr>
<td>4.2.1 partially molten</td>
</tr>
<tr>
<td>4.2.2 fusing powder mixture</td>
</tr>
</tbody>
</table>

Materials in SLS/SLM

**Materials in SLS/SLM**
Main binding mechanisms for metals

Metals

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering
3. Full Melting
4. Chemically Induced Binding

- 2.1 separate structural and binder particles
- 2.1.1 different binder and structural materials
- 2.1.2 composite particles
- 2.1.3 coated grains particles
- 2.2 no distinct binder and structural materials
- 2.2.1 single phase material
- 2.2.2 fusing powder mixture
- 2.1 single component single material
- 2.2 single component alloyed material
- 2.3 fusing powder mixture

Titanium

Steel

Main binding mechanisms for ceramics

Ceramics

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering
3. Full Melting
4. Chemically Induced Binding

- 2.1 separate structural and binder particles
- 2.1.1 different binder and structural materials
- 2.1.2 composite particles
- 2.1.3 coated grains particles
- 2.2 no distinct binder and structural materials
- 2.2.1 single phase material
- 2.2.2 fusing powder mixture
- 2.1 single component single material
- 2.2 single component alloyed material
- 2.3 fusing powder mixture

Alumina

Materials in SLS/SLM
Main binding mechanisms for composites

Composites (cermets and others)

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering
3. Full Melting
4. Chemically Induced Binding

- Different binder and structural materials
- Separate structural and binder particles
- Composite particles
- Coated grains particles
- No distinct binder and structural materials
- Single phase material partially molten
- Fusing powder mixture
- Single component single material
- Single component alloyed material
- Fusing powder mixture

Chapter 1 - Polymers: polymers types for SLS/SLM

Mainly thermoplastics:
- (Semi-)crystalline
- Amorphous

Thermoplastic consolidation:
- Partial or full melting

Occasionally thermosetters:
- Thermoplastics
- Chemical induced binding

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg</th>
<th>Tm</th>
<th>Crystalline</th>
<th>Amorphous</th>
<th>Thermosetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td></td>
<td></td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td></td>
<td></td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>PA6</td>
<td></td>
<td></td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td></td>
<td>Crystalline</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td></td>
<td></td>
<td>Amorphous</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TEMPERATURE

- Hard elastic, brittle
- Hard elastic, tough
- Weak elastic
- Viscous melt
- Viscous melt

Temperature (°C)
**Thermoplastics in SLS/SLM**

Mainly thermoplastics:
- (Semi-)crystalline
- Amorphous

Main SLS consolidation:
Partial or full melting

**Volume change (shrinkage):**

- Amorphous
- (Semi-)crystalline

**Temperature**

- $T_a$
- $T_g$
- $T_m$

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_a$</th>
<th>$T_g$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Heat resistance**

- Imidized
- Advanced engineering
- Standard

Materials in SLS/SLM
Differential Scanning Calorimetry (DSC)

DSC curve: melting & recrystalisation peaks

- DSC curve for PA12  (Source: University Erlangen)
**Important DSC features for SLS/SLM**

Melting consolidation: dependant on DSC curve

- Narrow melting range

![DSC curve for PA 12 and PA 6](image)

- Avoid overlapping heating & cooling peaks
- Avoid double peaks
- Influence molecular weight (viscosity)

**Polymers: other important features**

- Melt and re-crystallisation behaviour: DSC-curve
- Powder morphology and flowability
- Molecular weight
- Melt viscosity and flowability
- Oxidation (degradation)
- Etc.

![Melt Flow Index (MFI)](image)

- Orange peel surface texture
## Polymers: types and applications

<table>
<thead>
<tr>
<th>Polymer powder material</th>
<th>Application field</th>
<th>Example</th>
<th>Main properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Semi Crystalline Polymers e.g. PA-12</td>
<td>(Semi-)Rigid polymer parts</td>
<td></td>
<td>Long term useable</td>
</tr>
<tr>
<td>2 Amorphous Polymer e.g. PS</td>
<td>Investment Casting Lost patterns</td>
<td></td>
<td>Accurate Partially porous</td>
</tr>
<tr>
<td>3 Sacrificial Polymers used as binder e.g. PMMA</td>
<td>Metal or Ceramic Parts</td>
<td></td>
<td>Thermally degradable amorphous polymers</td>
</tr>
<tr>
<td>4 Filled Semi Crystalline Polymers e.g. PA-GF, PA-Cu</td>
<td>Parts with special properties</td>
<td></td>
<td>Long term useable Can withstand high loads</td>
</tr>
<tr>
<td>5 Elastomeric Polymers e.g. Polyester</td>
<td>Elastic parts</td>
<td></td>
<td>Long term useable</td>
</tr>
<tr>
<td>6 Polymer-Polymer Blends e.g. epoxy resin</td>
<td>Emerging Extreme Applications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 Thermo-setting Polymers e.g. epoxy resin</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Polymer 1: Semi-crystalline (e.g. PA12)

Partial or full melting of PA12

- Un-molten complete particle stuck to edge
- Un-molten particle core
- Fully molten particle (no core)

Source: Zarringhalam et al. (2006)

Loose un-sintered PA-12 powder

Tensile break surface showing some air voids

Source: Zarringhalam et al. (2006)
**Polymer 1: Semi-crystalline – DSC curves**

Comparison of DSC curves:
- PA12 for SLS (PA 2200)
- PA12 milled
- POM milled

Source: University Erlangen

**Polymer 1: Semi-crystalline (e.g. POM)**

Transmission light microscopy images of microtome sections

PA (rough surface)  
POM (smooth surface)

Source: University Erlangen
**Polymer 2: Amorphous (e.g. PS)**

**Partial melting**

**Low strength**: only partial consolidation

**Better accuracy**: no sudden shrink (jump) when solidifying (crystalline shrink at $T_m$)

![Relative Volume vs Temperature Graph](image)

- Amorphous
- Semi-crystalline

![Tensile break surface showing some air voids](image)

![Loose un-sintered PS powder](image)

**Polymer 3: Debindable polymers (e.g. amorph. PMMA)**

**Partial melting / LPS**

- Powder: debindable polymer binder + structural particles (metal or ceramic)
- Thermal debinding (depolymerisation) should occur in furnace at 350°-450°C, while not occurring during SLS
- Suited polymers: PMMA or MMA-BMA co-polymers
- May involve some cross-linkers (thermosets)

**Examples:**

- Steel (RapidSteel, Laserform): coated powder
- AW glass ceramics: mixed powder

Source: Dalgarno

![Green RapidSteel part](image)

![Powder mixture](image)

![Green part (i.e. after SLS)](image)

![Brown part (i.e. after debinding & firing)](image)
**Polymer 3: Debindable polymers (e.g. amorph. PMMA)**

- Injection mould inserts made by SLS of polymer coated steel particles, after debinding and infiltration with bronze

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**Polymer 4: Reinforced polymers (e.g. PA-GF)**

Partial melting / LPS

- Loose un-sintered PA-Glass powder
- Polyamide + Glass beads
- Tensile break surface showing some air voids

- Loose un-sintered PA-Al powder (30% Al)
- Polyamide + Alu beads
- Tensile break surface showing some air voids
**Polymer 4: Reinforced polymers (e.g. PA-Cu)**

Injection mold made from **Cu-filled Polyamide** and Polypropylene molded parts (injected at 2.76 MPa and 230°C)

Other:
- SiC-PA
- HA-HDPE
- HA-PA

---

**Polymer 4: Reinforced polymers (long fillers)**

Polyamide (nylon) with elongated filler

<table>
<thead>
<tr>
<th>Property</th>
<th>DF-M</th>
<th>3D PA</th>
<th>3D GF</th>
<th>3D AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>49.00</td>
<td>43.00</td>
<td>27.00</td>
<td>35.00</td>
</tr>
<tr>
<td>Tensile elongation %</td>
<td>5.00%</td>
<td>14.00%</td>
<td>1.50%</td>
<td>1.50%</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>5376</td>
<td>1586</td>
<td>4068</td>
<td>3960</td>
</tr>
<tr>
<td>HDT [1.82 Mpa]</td>
<td>165</td>
<td>95</td>
<td>134</td>
<td>137</td>
</tr>
</tbody>
</table>

Source: FHSG - Valspar
Polymer 5: Elastomeric polymer (e.g. polyester)

Partial melting

- Polyester-based elastomer

Green part (i.e. after SLS and without infiltration)

Part after infiltration with polyurethane

![Image of green part](image1.png)

![Image of part after infiltration](image2.png)

Materials in SLS/SLM

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Polymer 5: Elastomeric polymer (e.g. polyester)

Partial melting

- Polyester-based elastomer

Green part (i.e. after SLS and without infiltration)

Part after infiltration with polyurethane

![Image of shore A hardness vs. elongation](chart.png)

Shore A Hardness vs. Elongation %

<table>
<thead>
<tr>
<th>Material</th>
<th>Shore A (low)</th>
<th>Shore A (high)</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Materials in SLS/SLM
Polymer 6-7: Others (polymer blends, thermosets)

- **Polymeric blends**: Partial melting
  - Multiphase materials → tuned microstructure!
  - Example 1: mixed PA – HDPE (80/20, 50/50, 20/80 wt%)
  - Example 2: polymer 1 coated with low melting (thermoplastic) polymer 2 ($T_m<70^\circ C$, e.g. polyvinyl acetal, heptadecanoic acid,…)

- **Thermosetting materials**: Chemical binding
  - E.g. mixture epoxy-iron (by post-SLS epoxy infiltration)
  - Hydrogen bounds between polar $O^-$ from resin and $H^+$ on iron surface

\[
\text{Metal (Fe)} \quad \text{Active hydrogen} \quad \text{Hydrogen bond} \quad \text{Metal surface} \quad \text{Polar group}
\]

Polymers: Conclusion – Comparison Molding

- **Different classes of polymers covered**
  - Semi-crystalline
  - Amorphous
  - Debindable
  - Filled polymers
  - Elastomeric
  - Polymer-polymer blends
  - Thermosetting

- **Scope of applicable polymers still limited**
  - Still mainly PA (plain or filled)

- **Good, but no extreme properties**
## Chapter 2 - Metals

### Metals

#### Binding mechanism classification

1. **Solid State Sintering**
   - 2.1 different binder and structural materials
   - 2.1.1 separate structural and binder particles
   - 2.1.2 composite particles
   - 2.1.3 coated grains particles

2. **Liquid Phase Sintering**
   - 2.2 different binder and structural materials
   - 2.2.1 separate structural and binder particles
   - 2.2.2 composite particles

3. **Full Melting**
   - 3.1 single component
     - 3.1.1 single phase material
     - 3.1.2 partially molten
     - 3.1.3 fusing powder mixture
   - 3.2 multiple materials
     - 3.2.1 separated material
     - 3.2.2 mixed material

4. **Chemically Induced Binding**
   - 4.1 single component
     - 4.1.1 single phase material
     - 4.1.2 partially molten
     - 4.1.3 fusing powder mixture

---

### Metals: important features

**All type of consolidation possible:**
- SSS, LPS, Partial melting, Full melting, Chemical

**Important distinction:**
- Single material
- Multiple materials (separated/mixed, composite, coated, alloyed)

**Important criteria:**
- Phase and TTT-CCT diagrams
- Wetting
- Melt pool viscosity (versus temp.)
- Particle size distribution & shape
- Powder flowability
**Metals 1: Liquid Phase Sintering** (different materials)

**Binding mechanism classification**

1. Solid State Sintering
2. Liquid Phase Sintering Partial Melting
3. Full Melting
4. Chemically Induced Binding

**Metals 2: LPS / Partial melting** (no distinct materials)

**Binding mechanism classification**

1. Solid State Sintering
2. Liquid Phase Sintering Partial Melting
3. Full Melting
4. Chemically Induced Binding

**Fe-Fe₃P-Ni-Cu powder mixture**
**Metals 3: Full Melting** (e.g. Titanium)

### Binding mechanism classification

1. **Solid State Sintering**
   - 2.1.1 separate structural and binder particles
   - 2.1.2 composite particles
   - 2.1.3 coated grains particles
   - 2.1 different binder and structural materials
2. **Liquid Phase Sintering**
   - 2.2.1 single phase material partially molten
   - 2.2.2 fusing powder mixture
   - 2.2 no distinct binder and structural materials
3. **Full Melting**
   - 3.1 single component single material
   - 3.2 single component alloyed material
   - 3.3 fusing powder mixture
4. **Chemically Induced Binding**

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**Materials in SLS/SLM**

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**Pure Ti (CP Ti)**

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**Ti6Al4V**

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**Ti dental frame**

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**Metal 3: Full Melting** (e.g. Titanium)

### Binding mechanism classification

1. **Solid State Sintering**
2. **Liquid Phase Sintering**
   - Partial Melting
   - 3.1 single component single material
   - 3.2 single component alloyed material
   - 3.3 fusing powder mixture
3. **Full Melting**
4. **Chemically Induced Binding**

---

**Ti6Al4V**

---

**Materials in SLS/SLM**

---

<table>
<thead>
<tr>
<th>Ti6Al4V</th>
<th>SLM</th>
<th>Bulk annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [kg/m³]</td>
<td>4415</td>
<td>4430</td>
</tr>
<tr>
<td>Hardness [Vickers]</td>
<td>405</td>
<td>&gt; 350</td>
</tr>
<tr>
<td>Yields strength [MPA]</td>
<td>1125</td>
<td>&gt; 1035</td>
</tr>
<tr>
<td>UTS [MPa]</td>
<td>1250</td>
<td>&gt; 1035</td>
</tr>
<tr>
<td>Elongation [%]</td>
<td>6</td>
<td>&lt; 11</td>
</tr>
<tr>
<td>E modulus [GPa]</td>
<td>94</td>
<td>&lt; 114</td>
</tr>
</tbody>
</table>
**Metals 3: Full Melting (e.g. Fe alloys)**

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering - Partial Melting
3. Full Melting
4. Chemically Induced Binding

Comparison: SLM vs. bulk material for SS 316 (Source ILT)

Stainless steel 316
Fe-Fe3P-Ni-Cu powder mixture

---

**Metals 4: Chemical binding (e.g. Al, reinforced Cu)**

Binding mechanism classification

1. Solid State Sintering
2. Liquid Phase Sintering - Partial Melting
3. Full Melting
4. Chemically Induced Binding

Cu-based composite:

Cu + Ti + C → TiC + heat for fusing Cu

SLS of Aluminium:

Chemically bounded skeleton in N₂ atmosphere:

After infiltration with eutectic Al-13.8Si-4.7Mg infiltrant:

---
**Benchmark parts in Steel**

- sharp corners
- thin wall 0.25 - 1
- hole Ø 0.5 - 5
- sloping plane
- cylinder Ø 0.5 - 5
- overhangs
- rounded corner
- thin plane

50 x 50 x 9 mm³

**Density of benchmark parts in Steel**

50 x 50 x 9 mm³
**Accuracy of benchmark parts in Steel**

<table>
<thead>
<tr>
<th>Nominal dimension</th>
<th>Length 50 mm</th>
<th>Width 50 mm</th>
<th>Height 7 mm</th>
<th>Hole 1 ∅ 5 mm</th>
<th>Hole 2 ∅ 2 mm</th>
<th>Hole 3 ∅ 1 mm</th>
<th>Hole 4 ∅ 0.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process 1</td>
<td>50.59</td>
<td>50.22</td>
<td>7.05</td>
<td>5.03</td>
<td>1.96</td>
<td>Not built</td>
<td></td>
</tr>
<tr>
<td>Process 2</td>
<td>50.08</td>
<td>50.09</td>
<td>6.96</td>
<td>4.87</td>
<td>1.97</td>
<td>Badly built</td>
<td>Not built</td>
</tr>
<tr>
<td>Process 3</td>
<td>50.12</td>
<td>50.11</td>
<td>7.12</td>
<td>4.84</td>
<td>1.95</td>
<td>0.95</td>
<td>Not built</td>
</tr>
<tr>
<td>Process 4</td>
<td>50.78</td>
<td>50.73</td>
<td>7.12</td>
<td>4.67</td>
<td>1.72</td>
<td>Badly built</td>
<td>Not built</td>
</tr>
<tr>
<td>Process 5</td>
<td>50.16</td>
<td>50.18</td>
<td>7.03</td>
<td>4.83</td>
<td>1.77</td>
<td>0.90</td>
<td>Not built</td>
</tr>
</tbody>
</table>

1 = 3D Sys/DTM  
2 = Concept Laser  
3 = Triumph  
4 = MCP-HEK  
5 = EOSINT M

**Density of SLM parts in Titanium**

**SLM of Ti6Al4V**

- Laser power = 95 W
- Layer thickness = 30 µm
Accuracy of benchmark parts in Titanium

<table>
<thead>
<tr>
<th>Deviations measured - designed</th>
<th>mean</th>
<th>max</th>
</tr>
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<tbody>
<tr>
<td>x-direction</td>
<td>15</td>
<td>36</td>
</tr>
<tr>
<td>y-direction</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>z-direction</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>angles</td>
<td>0.51</td>
<td>1.33</td>
</tr>
<tr>
<td>diameters</td>
<td>24</td>
<td>36</td>
</tr>
</tbody>
</table>

Materials in SLS/SLM

Thank you for your attention