Development of partially water soluble binder system for ceramic powder Injection moulding

Thomas Hanemann, Oxana Weber
Outline

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4. Process chain of new developed feedstock system
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   4. Debinding and sintering
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Process chain Micro-PIM

Preparation of feedstock

Powder
Binder

Powder injection molding

Debinding

Sintering

www.mikropritzgiessen.de
Advantages of Micro-PIM

- Exploits established plastic micro replication technology for the realization of ceramic and metal microparts
- Enables multi-component fabrication
- Huge potential for automation
- Low cost fabrication method for ceramic and metallic microparts
- Technology close to industry

But: moulding is only a part of a complex process chain
Feedstock requirements - general

- Huge solid of at least 45 vol% (ceramic) or 60 vol% (metal)
- Average particle size should be smaller than a 10\textsuperscript{th} of the smallest structural detail
- Low viscosity @ moderate temperatures
- Simple and reproducible compounding
- No phase separation under large shear stress
- Good mold filling behavior
- High green stability
- Simple debinding and sintering
Feedstock requirements - micro

- Microsized parts often possess complex and fragile structures
- Structural aspect ratio can be higher than one
- High structural homogeneity required
- Near-net-shape structure necessary, mechanical postprocessing almost impossible
- Defect-free demolding
## Compounding of established feedstock systems

<table>
<thead>
<tr>
<th>Binder system</th>
<th>PE/Wax</th>
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<tbody>
<tr>
<td>Partial solubility</td>
<td>n-hexane</td>
</tr>
<tr>
<td>ceramic</td>
<td>ZrO$_2$ (bimodal), Al$_2$O$_3$, Si$_3$N$_4$, BaTiO$_3$, ATN</td>
</tr>
<tr>
<td>metal</td>
<td>17-4PH, 316L, Cu, Au, W, W-La$_2$O$_3$, WC-Co</td>
</tr>
</tbody>
</table>

- Torque recording kneader, extruder, shear-rolls
- Compounding temperature: 125-180°C
- Viscosity: 100-500 Pa s
Process chain of new feedstock system

Binder composition:
1. suitable additive selection
2. base viscosity adjustment

Ceramic or metal filler:
Particle characterization
(spec. surface area, particle size)

Binder system | PMMA/PEG
---|---
Partial solubility | water
Ceramic | ZrO₂
Metal | 17-4PH

Reactive feedstock compounding:
1. Accessible max. solid load
2. Compounding parameter

Feedstock postprocessing
1. Thermal polymerization
2. Pelletizing

Feedstock characterization
1. Melt viscosity
2. Real solid load

Micro injection moulding
1. Moulding parameter
2. Greenbody quality

Debinding
1. With/without solvent
2. Thermal

Sintering
1. Sinter parameter
2. Oven atmosphere

Polyethylenglycol (PEG)
Polymethylmethacrylat (PMMA)
Modified process chain

Compounding → Polymerization → Granulation

Thermal Debinding → Solvent Debinding → Injection Moulding
Reactive compounding

- MMA/PMMA reactive resin/phenanthrene as plastizizer
- PEG300 as water soluble component
- Polyethyleneglycolalkylether (Brij92/93) as surfactant
  - concentration 8.8 mg/m² filler surface area
- Microsized ZrO₂ (Tosoh TZ-3YS-E)
  - Average particle size: 0.45 µm
  - Specific surface area: 6.6 m²/g
  - Sinter density: 6.05 g/cm³
- Torque controlled dissolver (VMA: Getzmann AE03-C1)
- Compounding parameters
  - 25°C
  - 1000 rpm
  - 15 min
- Maximum measured torque < 1.2 Nm
Reactive compounding - zirconia load sweep

- Stable torque up to a zirconia load of only 33 vol%
- At higher solid loadings
  - pronounced evaporation of MMA due to evolved shear heat
  - insufficient wetting of the dissolver blade
Melt viscosity - zirconia load sweep

- Melt viscosity increases with zirconia load
- Melt viscosity drops with increasing temperature
- Stable feedstocks up to 36 vol% 

Solid load to small for powder injection moulding
Measurement of the effective zirconia load by combustion experiments

- Observed MMA-loss during reactive compounding
- Effective zirconia load significantly higher
  - Initial 36 vol% means effective 48 vol%

Solid load sufficient for powder injection moulding
Injection Moulding of test specimen

- Feedstock with (initial 33 vol%), effective 45 vol% zirconia processed
- Isothermal process control
- Green density 3.45 g/cm³ (57 % theoretical density of zirconia)
Debinding and sintering

- Two strategies:
  - Solvent (water) assisted (deionized water, 8 h, 25°C) plus thermal debinding
  - Direct thermal debinding
- Sintering

Temperature profile
Debinding and sintering

- Sinter densities almost identical
- Improved quality by using combined debinding

### Table: Sinter densities

<table>
<thead>
<tr>
<th>Debinding strategy</th>
<th>Density (g/cm³)</th>
<th>Theoretical density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent plus thermal debinding</td>
<td>5.98</td>
<td>98.1 ± 1.1</td>
</tr>
<tr>
<td>Thermal debinding</td>
<td>6.05</td>
<td>98.9 ± 0.2</td>
</tr>
</tbody>
</table>

Free space faced side

Solid substrate faced side

Greenbody, Solvent/thermal debinding, Thermal debinding
Conclusion and Outlook

- Successful use of environmental-friendly binder system was shown
- Waiving of solvent-assisted debinding possible
- Importance of interface chemistry
- Huge ceramic densities possible
- Replication of “real“ microsized parts
- Further extension to metal injection moulding
Acknowledgement

- Lisa Merklein for reactive compounding
- Peter Holzer for injection moulding