Predictive model applicable to water debinding of complex shape parts injection molded using commercial feedstock

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Ceramic Injection Molding

Industrial sector's concern: shaping of complex advanced ceramics parts
- Selection of competitive forming method(s)
- Low cost of processing and high end-product performance

CIM (CERAMIC INJECTION MOLDING) is more and more present on world markets.

Advantages:
- Suited for the production of complex ceramic parts with precision, speed, and repeatability.
- Less assembling and/or manipulation steps.

- 4 successive steps
  1. Plasticizing
  2. Injection
  3. Strengthening
  4. Ejection

What is a feedstock?

In the past:
- Formulation by ceramic producer
  - Proportion powder-additives
  - Nature of binder & plasticizer
  - Nature of powder
  - Nature of adjuvants
  - Composition and behavior of feedstock clearly known

Today:
- Existence of commercial feedstocks
  - Ready-to-use
  - Composition unknown
  - No detailed technical data
  - Composition and behavior of commercial feedstocks "unknown"
Disadvantage of CIM

Existence of a critical step:

Removal of the large amount of additives

Several debinding methods of CIM parts

- Classical thermal debinding
- Supercritical or catalytic debinding
- Solvent debinding
- Water debinding

- low cost
- environmental friendly

Recommendations of the supplier:

Debinding step
- 24h in water (25°C)
- thermal (HR: 20 to 2 °C / h)

Sintering
- 1600°C (HR: 130 °C / h)

Sound part

80*20*5 mm³

80*20*2 mm³

Damaged part
Swelling & Cracking

Necessity to predict the time needed to remove a maximum fraction of the soluble binder

As a function of geometry, temperature and immersion duration in water
Previous works

**Lin & German:**
- For an infinite geometry, the fraction of soluble binder remaining, \( \ln \left( \frac{1}{F} \right) = f(t) \) with \( t \) immersion time

**Shivashankar & German:**
- Extension of previous model for a finite geometry
  - Introduction of a new parameter: \( \frac{1}{\psi} \) (= \( S / V \)) length scale

\[
\ln \left( \frac{1}{F} \right) = \frac{\pi^2 D t}{\psi^2} + K
\]

Goal & approach

Elaborate a predictive model of the water debinding of complex molded parts, to ease thermal post treatments

**Parameters:**
- Geometry
- Immersion time
- Temperature

**Weight losses:**
- Measured
- Calculated

**Model validation:**
- Post-treatments
Experimental procedure

- **Preparation of samples**
  - Injected at 160°C (Arburg 350-90 A270D), Alumina feedstock (Al₂O₃).
  - Debound in stirred water at 25°C, 40°C et 55°C for varying immersion times.
  - Dried at 50°C during 48h.

### Simple shapes

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Bars</th>
<th>Cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>1.477</td>
<td>0.997</td>
</tr>
<tr>
<td>2.6</td>
<td>0.748</td>
<td>0.917</td>
</tr>
<tr>
<td>3.6</td>
<td>2.250</td>
<td>0.983</td>
</tr>
</tbody>
</table>

**Wide range of the length scale**

- 60x10xe
- Ø16xe

### Real complex shapes

<table>
<thead>
<tr>
<th>Component</th>
<th>Heat sink</th>
<th>Nozzle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/Ψ</td>
<td>0.731</td>
<td>0.822</td>
</tr>
</tbody>
</table>

Results and discussion
Influence of the temperature

- Estimation of maximum weight loss in water:
  \[ W_{\text{max}} \text{ (feedstock)} \approx 6\% \]

Fraction of soluble binder remaining in the green \((F)\) is expressed by:
\[
\ln \frac{1}{F} = \frac{\pi^2 D t}{\Psi^2} + K
\]

With \( \Psi = V / S \)

Influence of the temperature

Plot of \( \ln(1/F) \) against \( t/\Psi \) at different temperatures: \( \text{Al}_2\text{O}_3 \)

- \( 1/\Psi = 0.748 \)

2 stages observed:

1. **Dissolution controlled stage**
   - Binder just near the sample surface can dissolve quickly.
   - \( R_{\text{diss}} \): Dissolution of binder at binder water interface.

2. **Diffusion controlled stage**
   - Binder water interface moves inwards in the sample. Creation of a porous network within the green body.
   - \( R_{\text{diff}} \): Diffusion of the solutes in the porous paths.

Influence of the geometry

Evolution of Fraction binder removed for different values of \( 1/\Psi \):
\( \text{Al}_2\text{O}_3 \) at 40°C

- If \( 1/\Psi \) (S/V) is high
  - Thin parts
  - Large contact surface between soluble binder and solvent (water)
  - Kinetic of binder extraction is faster
Influence of the geometry

Plot of $\ln(1/F)$ against $1/\Psi$ for different values of $1/\Psi$:
$\text{Al}_2\text{O}_3$ at 40°C: Diffusion controlled stage

- Diffusion controlled stage ($T = 40°C$)

- Inter-diffusion coefficient

Using the Shivashankar-German model,

<table>
<thead>
<tr>
<th>$1/\Psi$ range</th>
<th>0.983 - 0.917</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inter-diffusion coeff D (cm$^2$·s$^{-1}$)</td>
<td>$6.16 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Elaboration of predictive model

- Inter-diffusion coefficient $D$:
  follows an Arrhenius law

\[ D = D_0 \exp\left(\frac{-E_{\text{act}}}{RT}\right) \]

as observed $K_2$ depends on temperature

\[ K_2 (T) = 0.0028 T - 0.673 \]

<table>
<thead>
<tr>
<th>Stage</th>
<th>$D_0$ (cm$^2$·s$^{-1}$)</th>
<th>$E_{\text{act}}$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion</td>
<td>$1.65 \times 10^5$</td>
<td>8.38</td>
</tr>
</tbody>
</table>
Validation of the predictive model

\[ \frac{1}{F} = 5.94 \cdot 10^{-2} \cdot \Pi^2 \cdot \exp\left(\frac{8380}{RT}\right) \cdot \left(\frac{1}{\Psi}\right) + (0.0028T - 0.673) \]

Heat sink

\[ 1/\Psi = 0.731 \]

Nozzle

\[ 1/\Psi = 0.822 \]

Microstructure evolution

30 min

50 h

Cross section of specimens partially water debinded at 40°C for 30 min & 50 h (1/\Psi = 0.748).

The « Shrinking Core » can be clearly observed.
Sintering behavior

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Apparent density (g/cm³)</th>
<th>1/f</th>
<th>Density (supplier's data) (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1h / 40°/ 3.6</td>
<td>3.61</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>1h / 40°/ 2.6</td>
<td>3.68</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>1h / 40°/ 1.6</td>
<td>3.80</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>50h / 40°/ 3.6</td>
<td>3.88</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>50h / 40°/ 2.6</td>
<td>3.93</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td>50h / 40°/ 1.6</td>
<td>3.93</td>
<td>11.1</td>
<td></td>
</tr>
</tbody>
</table>

- Water debinding at 40°C for 1 and 50 h
- Thermal debinding (HR : 1°C / min)
- Sintering at 1600°C (HR : 2°C / min) for 2 h

Conclusion

- The water debinding process depends on:
  - the immersion time t
  - the longer the immersion time t, the larger the amount of removed soluble binder
  - the temperature T
  - the evolution of dissolution and diffusion coefficient
- the length scale (1 / Ψ)
  - the higher the length scale (1 / Ψ), the shorter the immersion time needed

- Existence of two stages:
  - Dissolution controlled / Diffusion controlled
  - Creation of an interconnected porous network, facilitating subsequent thermal extraction of the insoluble binder
Conclusion

- Elaboration & validation of the predictive model:

\[
\frac{1}{F} \ln\left(\frac{1}{F}\right) = 5.94 \times 10^{-2} F^2 \cdot 2.11 \cdot \exp\left(-\frac{8380}{RT}\right) \cdot \left(\frac{t}{\gamma}\right) + (0.0028T - 0.673)
\]

- Sintering (preliminary) of simple specimens:
  - \(1/F < 1/F_{\text{lim}}\) → damaged parts
  - \(1/F > 1/F_{\text{lim}}\) → sound parts \((d = 3.93 \text{ g/cm}^3)\)

Methodology applicable to any kind of feedstocks

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Perspectives

- Estimate the minimal value of fraction of soluble binder remaining in the green \((1/F)\) to obtain sound parts irrespective of geometry

- Optimize the thermal debinding step depending on this previous value \((1/F)\)
Acknowledgement

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Questions

Thank you for your attention