Design of alumina bodies with directional porosity by a freeze-casting method

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INTRODUCTION

MANUFACTURE OF POROUS MATERIALS

FIRST POSSIBILITY

SPOUNGE IMPREGNATION

STARCH CONSOLIDATION

OTHER POSSIBILITY

FREEZE CASTING

SOAP BUBBLES → SURFACTANT
FREEZE-DRYING

Synthesis of nanopowders
Synthesis of mixed oxides
Synthesis of POROUS materials

Solution → Freezing → Freeze-Drying → Thermal treatment

Vacuum sublimation at low T

Porous, soft granules

Suspension → Freeze-Casting → Porous bodies

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FREEZE-CASTING

Suspensions

Organics

Camphene
Warm milling

Sublimation at \( T_{room} \)

Aqueous

Freezing

Sublimation under vacuum
\((T < 0^\circ C)\)

Ice formation and growth

Crystal size = \( f(T_{freezing},\text{additive}) \)

CRYOPROTECTOR

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FREEZE-CASTING

CRYOPROTECTOR

PVA
Glycerol

Decrease in $T_{\text{freezing}}$

Interaction with dispersant forming micelles

10 wt% -1.6°C
20 wt% -4.8°C
30 wt% -9.5°C

Bonding to water molecules

Ice crystallization
Open microstructure
Higher homogeneity
Cracking avoiding
Increased strength
OBJECTIVE

PREPARATION OF ALUMINA BODIES WITH ALIGNED POROSITY BY FREEZE-CASTING

Influence of the solid content of the starting suspension
Addition of glycerol as cryoprotector
Influence of freezing conditions

Pore size and distribution
Microstructure
EXPERIMENTAL

Suspension  
Al₂O₃ Condea HPA05 (USA), d₅₀ = 0.35 µm, Sₛ = 9.5 m²/g  
Dispersant: poly(acrylic acid, PAA (Duramax D3005, Rohm/Haas, USA)  
Ball milling 6h  
Cryoprotector, Glycerol

Procedure

Suspension  
Freezing  
Drying

Sintering

2°C/min: 250°C/30min  
5°C/min: 1500°C/2h  
10°C/min: 1200°C  
5°C/min: T_room

Suspension Freezing Drying Sintering

Characterization  
Flow behaviour (CR): Haake RS50 (sensor DC60/2)  
FE-SEM  
Mercury Intrusion Porosimetry  
Green and sintered densities

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EXPERIMENTAL

Directional Freezing

Bulk Freezing

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### EXPERIMENTAL CONDITIONS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content</td>
<td>20, 35, 50 vol% 50, 68, 80 wt%</td>
</tr>
<tr>
<td>Cryoprotector (Glycerol)</td>
<td>0, 10, 20 wt% (respect to water)</td>
</tr>
<tr>
<td>Freezing device</td>
<td>bulk, directional</td>
</tr>
<tr>
<td>Freezing rate</td>
<td>$\text{N}_2$ (l) (-198°C) instantaneous freezer (-20°C) slow</td>
</tr>
</tbody>
</table>
RHEOLOGY OF FREEZING SUSPENSIONS

EFFECT OF GLYCEROL AND SOLIDS LOADING

- 50 vol%
- 50 vol%/20 wt% glycerol
- 20 vol%
- 20 vol%/20 wt% glycerol

Stress (Pa)
Shear rate (s⁻¹)

- 20 wt% glycerol
- 20 vol%
- 35 vol%
- 50 vol%

Stress (Pa)
Shear rate (s⁻¹)
DIRECTIONAL FREEZE CASTING

EFFECT OF SOLIDS CONTENT

20 wt% glycerol

20 vol% 35 vol% 50 vol%

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DIRECTIONAL FREEZE CASTING

EFFECT OF SOLIDS CONTENT

20 wt% glycerol

Properties of sintered bodies

<table>
<thead>
<tr>
<th>Suspension (vol %)</th>
<th>Relative density (% TD)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>20 vol%</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>35 vol%</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>50 vol%</td>
<td>78</td>
<td>22</td>
</tr>
</tbody>
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DIRECTIONAL FREEZE CASTING

EFFECT OF CRYOPROTECTOR ADDITION

35 vol%

10 wt%  20 wt%

BETTER FORMATION OF CHANNELS
DIRECTIONAL FREEZE CASTING

EFFECT OF CRYOPROTECTOR ADDITION

35 vol%

Properties of sintered bodies

<table>
<thead>
<tr>
<th>Glycerol (wt %)</th>
<th>Relative density (% TD)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green</td>
<td>Sintered</td>
</tr>
<tr>
<td>10</td>
<td>31</td>
<td>55</td>
</tr>
<tr>
<td>20</td>
<td>39</td>
<td>58</td>
</tr>
</tbody>
</table>

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FREEZE CASTING

EFFECT OF FREEZING DEVICE

20 wt% glycerol

Directional

35vol%

Bulk

NO PREFERRED ORIENTATION
LOWER PORE SIZE

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FREEZE CASTING

EFFECT OF FREEZING DEVICE

20 wt% glycerol

35vol%

Properties of sintered bodies

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<td>Directional</td>
<td>39</td>
<td>58</td>
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<tr>
<td>Bulk</td>
<td>39</td>
<td>57</td>
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BULK FREEZE CASTING

EFFECT OF FREEZING RATE
20 wt% glycerol

Liquid nitrogen (-198°C) 35vol%

Freezer (-20°C)

SLOWER RATE LEADS TO LARGER ICE CRYSTALS

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BULK FREEZE CASTING

EFFECT OF FREEZING RATE

20 wt% glycerol

35 vol%

Properties of sintered bodies

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</tr>
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<td>N₂-liq</td>
<td>39</td>
<td>57</td>
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<tr>
<td>Freezer</td>
<td>31</td>
<td>59</td>
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CONCLUSIONS

Freeze-casting has been successfully used to shape porous bodies of alumina with aligned porosity in the direction of the ice growth.

The total porosity decreases as the solids loading increases.

Higher content of glycerol is necessary to achieve open, aligned pore channels.

Freezing device does not change the total porosity, but narrower pore size distribution is obtained for bulk freezing.

The higher is the freezing rate the lower is the pore size, although the total porosity is nearly the same.

Particles forming the inner walls of the pores or channels are well sintered.
THANK YOU VERY MUCH