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Freeze-casting to create micro-channels in La$_{0.66}$Ca$_{0.33-}$Sr$_x$Mn$_{1.05}$O$_3$

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Introduction

Freeze casting results in channels of widths of 10 to 100 µm, where the porosity depends on the solid load while the size of the channels depends on freezing conditions [3][4].

The figure on the right shows solid magnetic regenerators made of magnetocaloric materials of packed irregular particles and stacked plate geometries. A geometry in between – such as a micro-channel matrix – would be optimum.

Materials and methods

The standard freeze casting route is altered in two steps:

Dynamic and static freezing: Samples were frozen either statically at −98 °C or dynamically at −10 °C/ min.

Gelation freeze casting: Gelatin was added at 0.3 wt% (of solids) and left to harden before freezing.

Powders were used as received from Cer-Po-Tech and characterized as follows:

<table>
<thead>
<tr>
<th>$s$ (µm)</th>
<th>Density (g/cm$^3$)</th>
<th>Surface area (m$^2$/g)</th>
<th>$\theta$ (°)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>0.601</td>
<td>20.12</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>0.87</td>
<td>0.6491</td>
<td>17.62</td>
<td>0.34</td>
<td>8.70</td>
</tr>
<tr>
<td>0.075</td>
<td>0.6403</td>
<td>0.914</td>
<td>6.552</td>
<td>8.54</td>
</tr>
</tbody>
</table>

The Zeta potential reaches a plateau at the lower pH range, indicating that a stable slurry is achieved at pH 7. All slurries were thus prepared at pH = 7.

Conclusions and outlook

Antisotropic porosity in the form of lamellar channels where achieved in LCSM ceramics by freeze casting, with increased homogeneity and lower aspect ratios achieved by implementing dynamic freezing profiles and an additional gelation step, respectively. Thus, future work includes:

- X-ray tomography to establish 3D structure (i.e. pore connectivity, quantification of gelation)
- Increased control of freezing for homogenous macrostructure
- Detailed quantification of microstructure to establish correlation between processing (specifically freezing and sintering) and structure
- Structure of ceramics vs. performance as regenerator material in magnetocaloric refrigeration systems

Acknowledgement

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References

[2] T. Lei, K. K. Nielsen, and R. Bjørk, “Microstructural sensitivity of LCSM with respect to time at the moment of freezing (T=0) plotted as a function of height. The freezing front velocity decreases as the ice height increases due to increased thermal resistance. The lamellar pore size increases as the freezing front velocity decreases.

SEM images showing the cross section perpendicular and parallel to the freezing direction of 14 vol% LCSM frozen with no control of temperature. Scale bar indicates 100 µm.

Length and width of lamellar pores were determined by fitting an ellipse to individual pores in ImageJ. Pore size is here plotted as a function of height. Lamellar pore width is increased by a factor of 3, while the length is increased by a factor of 7.

A continuous measurement of temperature in four locations along the sample height yields the temperature change with respect to time at the moment of freezing (T=0) plotted as a function of height. The freezing driving force decreases along the height of the sample.

Results: Dynamic and static (gelation) freezing

Slimes of 14 vol% LCSM were freeze casted without control of temperature besides that of liquid N$_2$.

Static freezing results in a large increase in both pore width and length along the height of the sample whereas the increase is much smaller for the dynamic freezing.

The aspect ratios in the gelation freeze casted samples are smaller than the samples without gelatin indicating more circular pores, possibly due to reduced R-crystal formation during ice growth.

Results: Varying particle size

Slimes of 20 vol% LCSM where freeze casted by dynamic and static freezing profiles, with and without the addition of gelatin.

Static freezing results in a large increase in both pore width and length along the height of the sample whereas the increase is much smaller for the dynamic freezing.

The aspect ratios in the gelation freeze casted samples are smaller than the samples without gelatin indicating more circular pores, possibly due to reduced R-crystal formation during ice growth.

Background

In freeze casting, a ceramic aqueous suspension (1) is directionally frozen (2). The ice crystals are removed by sublimation (3) leaving directional voids or channels in the material which is then sintered to a solid (4).