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Christiansen, Cathrine D.; Nielsen, Kaspar K.; Bordia, Rajendra K.; Bjørk, Rasmus

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Accepted Article

The effect of gelation on statically and dynamically freeze-cast structures

Cathrine D. Christiansen^{a,§}, Kaspar K. Nielsen^a, Rajendra K. Bordia^b,
Rasmus Bjørk^a

^aDepartment of Energy Conversion and Storage, Technical University of Denmark,
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

^bDepartment of Materials Science and Engineering, Clemson University,
161 Sirrine Hall, Clemson, SC 29634-0871, United States

[§]Corresponding author e-mail: cadech@dtu.dk

Abstract

Freeze-casting is a technique used to produce structures with anisotropic porosity in the form of well-defined micro-channels throughout a sample. Here, this technique is used on the magnetocaloric ceramic $\text{La}_{0.66}\text{Ca}_{0.26}\text{Sr}_{0.07}\text{Mn}_{1.05}\text{O}_3$. We show that a dynamic freezing profile, where the temperature is decreased continuously at -10 K/min, results in homogenous, lamellar channels with widths of ~ 15 μm , while static freezing, where the temperature is kept constant at 177 K, results in channels of increasing size away from the initial ice crystal nucleation site. The effect of gelation before freeze-casting is also investigated. Gelation inhibits ice crystal growth, which significantly changes the morphology by making channel cross-sections less elongated, while additionally introducing more dendrites and ceramic bridges in the struc-

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ture. The latter significantly dominates the flow path through the gelated structures, affecting the calculated tortuosity, which increases to $\tau \approx 4$ when compared to non-gelated samples where calculated tortuosities are in the range of ~ 1.3 to ~ 3 . Finally, we present a systematic and automatic approach for evaluating channel and wall sizes and calculating tortuosities. This is based on analysis of images obtained by scanning electron microscopy using a continuous particle size distribution method and the TauFactor application in MATLAB®.

Key words: Freeze-casting; ice-templating; gelation-freeze-casting; directional porosity; magnetocaloric; gelation; static freezing; dynamic freezing

1 Introduction

Engineering of porous ceramics by freeze-casting has gained increased interest during the past 20 years^{1,2}, as it is an easy processing route to fabricate anisotropic, high porosity ceramics, polymers and metals.

Freeze-casting, or ice-templating, is a novel templating technique based on the anisotropic growth of ice crystals in, typically, aqueous suspensions upon directional freezing. Directional freezing is achieved by bringing one side of the suspension into contact with a cooling source, later on referred to as the cold side, creating a thermal gradient across the suspension. When ice crystals grow in a ceramic suspension with an appropriate thermal gradient they cause a segregation of ceramic particles resulting in a two-phase system of ice and ceramic. Removing the ice by sublimation followed by (partial) sintering results in a ceramic structure with anisotropic porosity in the form of directional macro-pores where the ice used to be. The dimensions of the macro-pores thus depend on the size of the ice crystals

and are typically of the order $\sim 1 \mu\text{m}$ to $\sim 100 \mu\text{m}$ ³⁻⁵. While water is the most common solvent, alternatives such as camphene⁶ or *tert*-butyl alcohol⁷ have been used successfully, however, with different solidification temperatures and altered morphologies. With no temperature control other than that of a specific coolant, the macro-pore dimensions are typically graded throughout the structures being smaller at the bottom than at the top. In addition, the porosity of freeze-cast structures is hierarchical having maintained micro-porosity within the walls^{1,8}. These physical properties make freeze-cast structures advantageous for e.g. biomedical applications^{9,10} or applications of limited thickness such as filters and ceramic support structure for e.g. membranes or fuel cells^{5,11,12}. However, for applications where the ceramic is a medium for oscillating flows of fluids or gasses in larger bodies, homogeneous channel sizes and consistent morphology are preferred^{13,14}.

In freeze-casting, the morphology of the pores very strongly depends on the freezing conditions; most notably is the conclusion that the faster the freezing front moves, the narrower will the resulting channels be³⁻⁵. Thus, controlling the freezing front velocity is equivalent to controlling the structural dimensions. Another possible way of controlling the morphology of the pores of a freeze-cast structure is to alter the chemical composition of the solvent and thus the physical properties of the solvent during freezing. One way of doing so is by gelation of samples prior to freezing, achieved by introducing a gelling agent, such as gelatin, into the suspension.

Previously, gelation has been used in gelcasting¹⁵ as a near-net-shaping technique for ceramic processing. Combining gelation and freeze-casting using gelatin was introduced by Fukushima *et al.*^{16,17}, who showed that initial gelation of samples completely alters the morphology of the pores while achieving complex shapes throughout the entire ceramic body. The gelated

freeze-cast structures have, however, primarily been used for processing of insulating materials¹⁶, membranes¹⁸ and biomedical purposes¹⁹, where the latter utilizes the hierarchical nature of freeze-cast structures, as previously mentioned. However, until now gelated freeze-cast structures have been processed using primarily static freezing profiles^{16–19}. For a static freezing profile the cold side is kept at a constant temperature below the freezing temperature of the solvent throughout the freeze-casting process. Static freezing profiles lead to a changing freezing front velocity during casting, resulting in structures with varying macro-pore sizes^{3–5}.

In this paper we investigate the effect of implementing dynamic freezing profiles, more specifically conditions where the temperature of the cold side is decreased linearly in time throughout the freeze-casting process. Dynamic freezing profiles lead to a more steady freezing front velocity^{3–5}. Here, we investigate the implementation of dynamic freezing profiles together with gelation, and the combined influence of these freezing conditions on the resulting porosity, and morphology of pores of the freeze-cast structures are reported. For the microstructural analysis a systematic and automated image quantification technique has been developed and used.

The approach of implementing static and dynamic freezing profiles and gelation prior to freeze-casting is carried out on $\text{La}_{0.66}\text{Ca}_{0.33-x}\text{Sr}_x\text{Mn}_{1.05}\text{O}_3$ (LCSM) ceramic powders. Ceramic processing — and thus freeze-casting — of LCSM powders is similar to that of LSM powders used by Lichtner *et al.*^{5,20}, and has previously been reported by the authors of this paper²¹. In addition, LCSM is magnetocaloric, meaning that the temperature of the material will change if a magnetic field is applied²². The Curie temperature, which is the transition temperature between the ferromagnetic and paramagnetic states, of LCSM can be conveniently tuned around room temperature

by varying the amount of dopants²³ — i.e. the ratio between calcium, Ca, and strontium, Sr — making it applicable as regenerator material in magnetic refrigeration²⁴. In this context, freeze-casting offers the possibility of engineering monolithic LCSM structures with aligned, directional porosity in the form of macro-pores — also referred to as micro-channels — a geometry which is advantageous for heat transfer²⁵.

2 Materials and methods

2.1 Powder properties and preparation of ceramic suspensions

Ceramic suspensions for freeze-casting were prepared from 20 vol% powders of $\text{La}_{0.66}\text{Ca}_{0.26}\text{Sr}_{0.07}\text{Mn}_{1.05}\text{O}_3$ (LCSM, CerPoTech, Norway) in distilled water, with the addition of 2.5 wt%, relative to the ceramic powder, of DURAMAX™ D-3005 (Rohm and Haas, Dow Chemical, United States) as dispersing agent.

The specific surface area and density of the powder were determined by the BET method using a Nova 4000e (Quantachrome Instruments, United States), and by gas pycnometry using an AccuPyc II 1340 (Micromeritics, United States), respectively. The particle size distributions of both raw powder and milled suspensions were determined using an LS 13 320 Laser Diffraction Particle Size Analyser (Beckman Coulter). Additionally, the surface charge as a function of pH was measured using a Zeta potentiometer coupled with a pH probe, Zeta Potential Analyzer (Colloidal Dynamics, United States), and determined by titration of an aqueous suspension of 0.9 wt% powder with 0.1 M NaOH and 0.1 M HCl. Powder properties are summarized Table 1.

Measurements of the surface charge show that the zeta potential reaches a plateau at the lower pH range, indicating that a stable slurry is achieved at $\text{pH} < 7$. All slurries were thus adjusted from a $\text{pH} \sim 8.5$ to $\text{pH} \sim 6$ by dropwise addition of nitric acid. In order to achieve a sufficient dispersion of powders, slurries were mixed by sonication using a homogenizer (S-450A, Branson Ultrasonics, United States) for 2x30 seconds and subsequently homogenized using a low energy ball mill with zirconia balls with $\phi = 10$ mm for 24 h. Thereafter, 1.5 wt%, relative to the ceramic powder, of DURA-MAXTM B-1022 (Rohm and Haas, Dow Chemical, United States) was added as binder and mixed for additional 30 minutes using a low energy ball mill. Suspensions were de-aired under low vacuum for a few minutes immediately before casting.

In order to investigate the effect of gelation of samples, an additional gelation step was implemented for some samples prior to freeze-casting. Gelation was achieved by preparing a solution of gelatin (granular, type A from porcine, lab grade, Ward's Science, United States), corresponding to 0.3 wt% relative to the ceramic powder, by dissolving granular gelatin in distilled water and stirring at 323 K using a magnetic stirrer. The suspension of powder and dispersant, prepared as described above without the addition of binder, was also heated to 323 K and the gelatin solution was mixed with the suspension by continuous stirring while maintaining the temperature in order to avoid premature hardening of the gelatin. The suspension was then transferred to a mould closed at the bottom using a thin sheet of aluminum foil attached by vacuum grease, and left to harden overnight at 278 K. The samples were subsequently left at ambient conditions to reach an equilibrium temperature with the surroundings before freeze-casting.

The relative amount of gelatin powder was chosen such that the sus-

pension just loses fluidity at ambient conditions after hardening overnight at 278 K. The formed gel network thus offers an increased viscosity or gel strength²⁶ for stabilizing the suspension and provides an additional step of net-shaping if desired¹⁶. However, in the current work, the gel network was applied to inhibit the ice crystal growth and thereby modify the pore morphology.

2.2 Freeze-casting procedure

Samples were frozen directionally at static and dynamic temperature profiles using a freeze-casting set-up previously described by Lichtner *et al.*^{20,27}. The set-up consisted of a large copper rod with $\varnothing = 76$ mm immersed in a bath of liquid nitrogen. A large interface between copper and liquid nitrogen achieved by fins cut into the copper rod provided increased temperature control, a faster freezing of samples and allowed for manual control of the freezing rate, by controlling the amount of liquid nitrogen in the bath. The temperature of the copper rod was monitored by the application of a K-type thermocouple. Cylindrical acrylic moulds of inner and outer diameter of 18 mm and 45 mm, respectively, were directly mounted on the top of the copper rod using vacuum grease while the top of the moulds were left open to ambient conditions. The large thermal mass of the copper rod and the thick walls of the acrylic mould with high thermal resistance ensured continuous freezing conditions and minimal heat exchange with the surroundings. Samples were frozen either dynamically or statically:

Dynamic freeze-casting of samples was achieved by manually adjusting the level of liquid nitrogen resulting in a freezing rate of -10 K/min. The de-aired suspension was poured into the mould and the temperature was decreased continuously from ambient. The freezing rate was kept

constant during the entire freezing procedure.

Static freeze-casting of samples was achieved by placing the copper rod in a cooling bath of liquid nitrogen and acetone. The acrylic mould was closed at the bottom using a thin sheet of aluminum foil attached by vacuum grease. The mould containing a de-aired suspension was thus transferred to the copper rod when this had reached a steady temperature of 177 K. Due to the large thermal mass of the copper rod, the temperature of the rod did not change significantly during freezing of samples and was thus assumed to be constant resulting in a static freezing.

After freeze-casting, ice was removed from the samples by sublimation in a freeze drier while the samples were still in their moulds (0.200 mBar, 223 K, FreeZone 2.5, Labconco) for at least 24 h. Dried samples were subsequently sintered in air at 1423 K for 3 h (heating rate of 2 K/min) with an initial burnout of organic additives at 723 K for 4 h.

2.3 Structure characterisation and quantification

Ceramic samples were prepared for mechanical handling and structural analysis by infiltration with epoxy (EpoFix, resin and hardener, Struers ApS, Ballerup, Denmark). Epoxy infiltrated samples were cut in half parallel to the freezing direction and one half was then sliced perpendicular to the freezing direction in thicknesses of 2 mm. These were then polished and coated with a ~ 12 nm thick carbon layer. Images of the perpendicular and parallel cross-sections of the samples were obtained using a scanning-electron microscope (SEM, TM3000, Hitachi High-Technologies). The microstructure of samples was investigated as a function of sample height, that is, the vertical distance — parallel to the freezing direction — from the bottom of the

sample and to the specific point of interest. Three images were obtained at each cross-section of interest, both for the parallel cut samples and for the perpendicular cut samples, in order to realize a statistically significant data set.

The macro-pores of the samples will in the following be referred to as micro-channels, as a fluid can be envisioned to flow through these. The micro-channels in the ceramic samples were characterised by analyzing SEM images using an image analysis software developed in MATLAB® (The MathWorks, Inc.). First the SEM images were binarized using a threshold value, as shown in Figure 1a). The analysis then depends on whether parallel or perpendicular cross-sections, with respect to the freezing direction, are investigated:

For SEM images of cross-sections perpendicular to the freezing direction, the size of the channels or walls are estimated by a continuous particle size distribution method. This is done by fitting circles of increasing size in every point in all channels (or walls) in a binarized image, determining the largest circle that can be fitted within all points in the channels (or walls), yielding a direct measure of the size of the channel (or wall)²⁸. The radius of these fitted circles are shown for the channels and the walls in Figures 1b) and 1c), respectively. As can be seen from the images, the above procedure results in a distribution of fitted circles throughout the SEM image. The average channel or wall diameter can then be calculated from this distribution. Additionally, macro-porosities, or channel-porosities, were estimated from the binarized images. SEM images used for estimating the channel and wall sizes were obtained at magnifications of x100 – x500. We found that the analysis of channel and wall sizes were independent of magnification in this range.

For some samples aspect ratios of the cross-section of the channels were also determined. This was done by manually fitting ellipses to channels in ImageJ and then calculating the ratio between the minor and major axis. For the relevant samples approximately 100 channels at a sample height of 6 mm was fitted with ellipses to determine the average aspect ratio.

For SEM images of cross-sections parallel to the freezing direction, the quality of the structure in terms of allowing a fluid to pass through can be estimated. This is done by calculating the tortuosity, τ , of the channels. Tortuosity is a measure of the curviness of channels, in this case, evaluating the ratio between the direct distance across a cross-section and the distance across the same cross-section through a channel. A factor of $\tau = 1$ corresponds to a direct flow path, while the greater the tortuosity the greater the curviness or skewness of the channels. Tortuosity was calculated using the TauFactor application²⁹ in MATLAB® (The MathWorks, Inc.). The software calculates the tortuosity in 2D from SEM cross-sectional images instead of the more intricate and time consuming procedure of doing a 3D X-ray tomography analysis of entire samples^{28,30,31}. However, calculating tortuosity from 2D cross-sections requires considerations about the magnification of analyzed SEM images. A too large magnification results in very few channels per image, while a too small magnification results in closed pores. The lamellar channels of freeze-cast structures have previously been shown to be arranged in domains of varying orientations and angles relative to the freezing direction^{20,32}, as is also evident from the perpendicular cross-sections in Figure 2, resulting in what appears to be closed pores in the parallel cross-section images.

We found that images obtained at different sample heights at a magnification of x500 met the aforementioned criteria while still representing and

Figure 1: Processing of SEM images obtained from cross-sections perpendicular to the freezing direction in order to estimate channel and wall sizes. (a) Binarized SEM image, where white indicates ceramic walls and black is voids or channels. Circles are fitted to either the channels (b) or walls (c), with the fitted circle radius indicated by the colorbar.

maintaining general channel structure characteristics in form of wall morphology, skewness of channels and width of channels and walls. Thus, tortuosity was calculated parallel to the freezing direction across cross-sectional areas of $331 \times 248 \mu\text{m}$.

3 Results & discussion

Dynamic and static freezing conditions both result in anisotropic macroporosity in the form of micro-channels running along the freezing direction. The cross-section of each channel is ellipsoidal, giving an overall lamellar morphology, and the channels are ordered in domains of various orientations, as is evident on Figure 2. The porosity is hierarchical with macroporosity in the form of channels and microporosity in the ceramic walls, where the total porosity of non-gelated freeze-cast samples are $\sim 65\%$ while the gelated samples have a total porosity of $\sim 70\%$.

Introducing an initial gelation of the solvent by adding gelatin and leaving it to harden causes the medium in which the ice grows to change, thereby

Figure 2: SEM micrographs of cross-sections perpendicular and parallel to the freezing direction at sample heights of 6 mm and 6 ± 2 mm, respectively. White areas are ceramic walls while black areas are porosity in the form of lamellar, ellipsoidal channels.

changing the final morphology of the ice crystals and thus the resulting pores^{16,18,19,33}. While the macro-porosity of the gelated structures are still lamellar and the perpendicular pore shape is overall ellipsoidal, as is evident from Figure 2, the general morphology is significantly different.

3.1 Characterising and quantifying morphology

Various approaches have been taken to characterise and quantify morphology of freeze-cast microstructures during the past 20 years of increased interest in these porous materials. Generally, pore and wall sizes are measured in optical images or SEM micrographs of perpendicular cross-sections. Additionally, for lamellar morphologies the periodicity can be quantified by the structure wavelength, which is determined as the sum of the width of a channel and the width of the adjacent wall in a perpendicular cross-section³. Anisotropy of pores is usually evaluated by simple visual comparison between perpendicular and parallel cross-sections. Low tortuos-

ity of macro-pores is often claimed as a characteristic for freeze-cast structures^{11,12,29,34,35}, but is rarely calculated and evaluated with respect to freezing conditions. Miller *et al.*⁶ calculated tortuosities, however, only for static freezing conditions and only at one sample height.

Here we evaluate the tortuosity dependence on static and dynamic freezing conditions, and show that tortuosity calculations in 2D, in combination with automatic detection and evaluation of channel and wall sizes, can be used to quantify and evaluate the microstructure and homogeneity of channels in a freeze-cast material. To maintain an automatic, fast and reproducible workflow for analysis of a large quantity of SEM micrographs for morphological characterisation of freeze-cast structures, MATLAB® has been used.

3.2 Size distributions of micro-channels

Analyzing the SEM micrographs of cross-sections perpendicular to the freezing direction of freeze-cast structures as described in Section 2.3 yields a distribution of fitted circle sizes as shown in Figure 3. Only results from analysis of pores at the top (sample height of 8 mm) and bottom (sample height of 2 mm) of samples are shown in order not to clutter the plot.

As is clear from Figure 3, the pore size distributions, for all structures except the dynamically frozen structure without gelatin, are shifted towards larger channel sizes from bottom to top indicating a conical shape of channels, the width of channels being smaller at the bottom than at the top. Average channel and wall sizes are estimated by averaging the distributions of fitted circles weighed by area at each perpendicular cross-section. This is done for a range of sample heights, i.e. not just those shown in Figure

Figure 3: Size distribution of circles fitted to pores of cross-sectional SEM images. Only distributions at cross-sections at the top (sample height of 8 mm) and bottom (sample height of 2 mm) of freeze-cast structures are shown here. The arrows indicate the change going from the bottom to the top of the sample.

3. The average channel and wall size, as a function of distance from the cold finger, for both statically and dynamically frozen samples, as well as for non-gelated and gelated samples, are shown in Figure 4. As can be seen from Figure 4a) freeze-cast structures frozen using a static freezing profile of 177 K have inhomogeneous microstructure, where both channel size and wall size increase along the sample height. When the temperature of the

cold finger is static the suspension will initially freeze very fast. As the freezing front moves further away from the cold finger, due to low thermal resistance of the frozen ceramic, the temperature gradient at the freezing front decreases which reduces the freezing kinetics, i.e. the freezing front velocity, giving the ice crystals more time to grow perpendicular to the freezing direction. Larger ice crystals result in larger channel and wall sizes. These results are in accordance with previous studies correlating the channel size to the velocity of the freezing front, where the channel size increase with a decrease in freezing front velocity³⁻⁵.

However, while the channel sizes of the statically frozen structures increase by a factor of five from bottom to the top, the dynamically frozen structures maintain a channel size of $\sim 15 \mu\text{m}$ all the way through for the non-gelated samples. By implementing a dynamic temperature profile of -10 K/min the decreasing temperature gradient across the freezing front is compensated and presumably maintained during the complete freezing, resulting in steady freezing kinetics, i.e. a constant freezing front velocity, and thus in homogenous channel and wall sizes all the way through the freeze-cast structures.

The above reasoning moreover explains the intersection of channel sizes in Figure 4a) at a sample height of 8 mm, after which channels in statically frozen structures are larger than those in dynamically frozen structures. Eventually, the freezing kinetics of the statically frozen samples will be slower than at the equivalent height of dynamically frozen samples resulting in increasing ice crystal growth and thus larger channels in the final ceramic.

The estimated wall sizes follow the same trend as the channel sizes, although slightly larger. Regarding gelated samples, however, here the dy-

Figure 4: Channel and wall size as a function of distance from the cold finger (sample height) of freeze-cast structures frozen under static ($\diamond$) and dynamic freezing ($\square$) profiles without (a) and with (b) gelatin. SEM insets are of cross-sections perpendicular to the freezing direction at a sample height of 2 mm (bottom) and 8 mm (top), where the scale bar indicates 100 μm .

dynamic freezing profiles do not result in a homogenous structure. Moreover, the variation in the channel size for dynamically frozen structures is less than that for static frozen structures. The reason for this is discussed subsequently in Section 3.4.

3.3 Tortuosity of micro-channels

A similar conclusion, as for the size distribution, can be reached when evaluating the tortuosity of the structures frozen without initial gelation.

Tortuosity can be directly correlated to the nature of ice crystal growth under the conditions described in Section 2.2. The growth of ice crystals in ceramic suspensions during freeze-casting has previously been observed by *in-situ* X-ray radiography^{36,37}. Upon freezing, rapid nucleation takes place at the bottom copper surface forming ice crystals that grow in random directions. This is the isotropic region with no resulting directional porosity. Eventually, ice crystals growing along the direction of the temperature gradient are favoured, resulting in a region of aligned crystals. This region is referred to as the steady state region or the anisotropic region. In this region, aligned, lamellar ice crystals are arranged in domains of various orientations, resulting in the equivalent inverse, aligned, lamellar channels evident on the perpendicular cross-sections in Figure 2. The larger and more aligned the ice crystals are, the larger and straighter will the resulting channels be, leading to calculated tortuosities that are smaller.

The calculated tortuosities of micro-channels in freeze-cast structures frozen statically are shown in Figure 5. As can be seen from the Figure, samples frozen without an initial gelation step, Figure 5a), have a decreasing tortuosity along the sample height, while it is almost constant for the dynamically frozen structures. Based on tortuosity and channel sizes determined from SEM micrographs, implementing dynamic freezing profiles thus increases the morphological homogeneity of non-gelated freeze-cast structures, making them almost completely homogenous with respect to channel size and tortuosity.

While calculated tortuosities of non-gelated samples thus reflect freezing

Figure 5: Calculated tortuosities, τ , as a function of distance from the cold finger (sample height) of freeze-cast structures frozen statically and dynamically. Tortuosity is calculated from cross-sections of $331 \mu\text{m} \times 248 \mu\text{m}$ parallel to the freezing direction. Three cross-sections have been evaluated at each sample height. Results of both non-gelated (a) and gelated samples (b) are shown.

conditions, tortuosity for the gelated structures, however, is seen to have significantly larger error bars and also no clear trend is seen in the results. The reason for this will be discussed in the following section.

3.4 Morphology of gelated structures

As is evident from Figure 2, the channels of gelated freeze-cast structures — similar to those without gelation — are lamellar and the cross-sections are ellipsoidal, however, the aspect ratio decreases when comparing the non-gelated samples, to the gelated samples in Table 2. The channels of the gelated samples thus become less ellipsoidal, converging towards a more cylindrical shape, as previously described by Fukushima *et al.*²⁶. The change in morphology of the channels is likely due to the increased resistance the growing ice crystals meet due to the gel network making it harder for the crystals to push aside suspended particles.

Another plausible consequence of the resistance from the gel network can be seen in the higher magnification micrographs in Figure 6a), where the walls seem slightly less dense in the gelated freeze-cast structure. During freeze-casting the formation of ice crystals pushes the suspended particles together causing these to segregate into what will become the walls of the structures upon drying and sintering. It is possible that the gel network inhibits this segregation to some extent during the casting process, resulting in a less dense packing of particles in the walls of the gelated structures when comparing to the non-gelated structure in Figure 6b). In addition, the estimated channel-porosities of gelated freeze-cast structures are lower than those of non-gelated samples as seen in Table 2 even though the total porosity of gelated samples is larger than non-gelated samples. Moreover, the macro-porosity was found to not vary significantly throughout the length of the samples.

While the implementation of a dynamic freezing profile — compared to static freezing — significantly changes the dimensions of the channels along the sample height for non-gelated structures, resulting in more homogenous

channel sizes and tortuosities, as evident from Figures 3, 4 and 5, this is not the case for gelated structures. Both statically and dynamically frozen gelated structures are inhomogeneous in channel size as can be seen in Figure 4b), where an increasing channel and wall size along the sample height is seen. It is especially remarkable that the channel sizes for the gelated samples are not homogenous throughout the sample, as is clear from Figure 4b), even though the dynamic freezing profile is used. This could be due to the altered structure of the gelated freeze-cast sample, which is more unstructured than the corresponding standard freeze-cast sample. The significant difference in internal structure, or morphology, is clearly seen in Figure 5 showing the tortuosity of the respective samples. The larger tortuosity of the gelated samples reveal a somewhat more chaotic morphology which is thought to slightly decrease the thermal conductivity of the sample. Hence, throughout the length of the sample the freezing conditions change due to an increasing thermal resistance resulting in larger channels at the top of the sample. However, the effect is small as the channels are seen only to increase in size in the latter part of the sample. A direct measurement of the freezing front velocity during casting of both standard and gelated samples could clarify this assumption, however, with the present freeze-casting set-up where only visible tracking of the freezing front is possible[†] this was impossible due to the color (or lack thereof) of LCSM powders. Additionally, clarifying the altered freezing kinetics of gelated samples could then lead to a further tuning of dynamic freezing conditions — e.g. implementation of exponential or stepwise dynamic temperature profiles — which might prove as a way of engineering homogeneous, gelated freeze-cast structures.

The resulting pores in the freeze-cast gelated structures are, despite the

[†]See Lichtner *et al.*⁵, Figure 1

change in morphology and homogeneity, in the same size range as the standard freeze-cast ones. Meanwhile, the calculated tortuosities of structures frozen with an initial gelation step, Figure 5b), are generally larger than non-gelated structures and not directly correlated with sample height or channel size, but rather, scattered around $\tau \approx 4$ inconsistently.

The variability in the channel size and calculated tortuosity is partly due to the presence of dendrites and ceramic bridges across channels. As can be seen on the horizontal cross-sections in Figure 6a), ceramic bridges connect channel walls across the pores, while dendrites results in an obviously higher surface roughness than non-gelated structures when comparing parallel cross-sections in Figure 6a) and 6b). Bridges and dendrites increase the overall curviness of channels. For gelated freeze-cast samples, the finer scale contributions of dendrites and bridges to the calculated tortuosity overshadow that of the size and skewness of the channels.

Gelation thus provides an obstacle in fine-tuning and specific engineering of structures if one has a specific channel size in mind and a need for homogeneous, low tortuosity channels. It does, however, provide a way of altering the morphology of channels in freeze-cast structures, making the channels less ellipsoidal, more tortuous and more connected. These types of microstructures could have other advantages and applications. Specifically, it has been shown that the bridges between pore channels have a significant effect on the mechanical properties of freeze-cast materials^{20,38}.

4 Conclusion

Freeze-casting of ceramic suspensions, with and without gelation prior to freezing, of powders of the magnetocaloric LCSM ceramic results in rigid ceramic structures with anisotropic macro-porosity in the form of micro-

Figure 6: SEM images of cross-sections perpendicular and parallel to the freezing directions of a gelated (a) and a non-gelated (b) sample, both frozen dynamically at -10 K/min. Perpendicular and parallel cross-sections are at sample heights of 6 mm and 6 ± 2 mm, respectively. Higher magnification micrographs show the rougher nature of the wall surface of gelated structures in the form of dendrites and ceramic bridges connecting the walls of the channels. In addition, the walls of the gelated sample appear less dense than those of the non-gelated sample.

channels running along the freezing direction. The perpendicular cross-section of channels are ellipsoidal giving an overall lamellar geometry. Channel and wall sizes were quantified using an automated approach for analysis of 2D SEM micrographs obtained on cross-sections perpendicular and parallel to the unidirectional freezing direction. The microstructure was examined as a function of distance from the cold finger for both static and dynamic freezing conditions for samples with and without partial gelation. For non-gelated samples, static freezing at 177 K led to structures with channels of increasing size along the sample height, being $5 \mu\text{m}$ at the bottom and $20 \mu\text{m}$ wide at the top. However, dynamic freezing conditions, where the cold finger was cooled at -10 K/min, resulted in channels of homogenous size throughout the sample with a channel size of $\sim 15 \mu\text{m}$.

Implementing an initial gelation step prior to freezing inhibits ice crystal growth during the casting process, significantly changing the morphology, making the cross-section less ellipsoidal and introducing more dendrites and ceramic bridges. Both statically and dynamically frozen structures had channels of increasing size along the sample height, ranging from 10 μm to 25 μm for static structures and from 10 μm to 15 μm for dynamic structures.

The calculated tortuosity of non-gelated structures followed the trend of the channel sizes. For statically frozen samples, tortuosity decreased from $\tau = 3$ at the end close to the cold finger to $\tau = 1.5$ at the other end. For dynamically frozen samples, the tortuosity was constant at $\tau \approx 1.3$ throughout the sample. For gelated samples the calculated tortuosities at various sample heights showed significant variation around $\tau \approx 4$. This is attributed to the increased presence of dendrites and ceramic bridges infiltrating the pore space and dominating the flow path through the structures.

Freeze-casting using dynamic freezing profiles hold the promise of a processing route with the ability to control and optimize channel size and tortuosity of homogenous structures, yielding high tunability of ceramics for applications where the ceramic is a medium for e.g. fluid flow and heat transfer. Partial gelation of the slurry prior to freeze-casting provides another process variable to control and optimize the porous structure. However, further optimization of the slurry and the dynamic freezing conditions is needed to obtain homogenous microstructures using this approach. In some applications, the bridges spanning the pore space may be desirable for e.g. optimized mechanical strength or increased tortuous flow.

Supporting data

SEM micrographs are provided as supporting data, doi: 10.11583/DTU.7813523

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List of figures

Figure 1: Processing of SEM images obtained from cross-sections perpendicular to the freezing direction in order to estimate channel and wall sizes. (a) Binarized SEM image, where white indicates ceramic walls and black is voids or channels. Circles are fitted to either the channels (b) or walls (c), with the fitted circle radius indicated by the colorbar.

Figure 2: SEM micrographs of cross-sections perpendicular and parallel to the freezing direction at sample heights of 6 mm and 6 ± 2 mm, respectively. White areas are ceramic walls while black areas are porosity in the form of lamellar, ellipsoidal channels.

Figure 3: Size distribution of circles fitted to pores of cross-sectional SEM images. Only distributions at cross-sections at the top (sample height of 8 mm) and bottom (sample height of 2 mm) of freeze-cast structures are shown here. The arrows indicate the change going from the bottom to the top of the sample.

Figure 4: Channel and wall size as a function of distance from the cold finger (sample height) of freeze-cast structures frozen under static ($\diamond$) and dynamic freezing ($\square$) profiles without (a) and with (b) gelatin. SEM insets are of cross-sections perpendicular to the freezing direction at a sample height of 2 mm (bottom) and 8 mm (top), where the scale bar indicates 100 μm .

Figure 5: Calculated tortuosities, τ , as a function of distance from the cold finger (sample height) of freeze-cast structures frozen statically and dynamically. Tortuosity is calculated from cross-sections of 331 μm x 248 μm parallel to the freezing direction. Three cross-sections have

been evaluated at each sample height. Results of both non-gelated (a) and gelated samples (b) are shown.

Figure 6: SEM images of cross-sections perpendicular and parallel to the freezing directions of a gelated (a) and a non-gelated (b) sample, both frozen dynamically at -10 K/min. Perpendicular and parallel cross-sections are at sample heights of 6 mm and 6 ± 2 mm, respectively. Higher magnification micrographs show the rougher nature of the wall surface of gelated structures in the form of dendrites and ceramic bridges connecting the walls of the channels. In addition, the walls of the gelated sample appear less dense than those of the non-gelated sample.