Nucleation-controlled freeze casting of preceramic polymers for uniaxial pores in Si-based ceramics

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Abstract

A grain-selection template was applied to freeze casting to control nucleation of pore-forming crystals and achieve ceramics with highly aligned pore structures. A polymethylsiloxane preceramic polymer was freeze cast with cyclohexane as a solvent to produce dendritic pores in SiOC. Image analysis and permeability measurements were performed to quantify the influence of various templates on sample properties. Results show that templates increased the percentage of porosity aligned along the freezing axis, from 13.9% without a template to 92.6% with an optimal template. The Darcian permeability constant increased by more than 6-fold, from 3.4×10^{-12} to $2.1 \times 10^{-11} \text{ m}^2$.

Keywords: porous material; ceramics; directional solidification; casting; ice templating

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Ceramics with directionally aligned pores are sought after in applications such as catalyst supports, filtration membranes, and electrodes due to their ability to tailor flow and mechanical properties along a particular direction [1]. Despite this demand, precise control of pore structure has continuously been a challenge for ceramic materials. The most commonly used processing techniques for porous ceramics include direct foaming, replica templates, and sacrificial beads, however these techniques struggle to generate high-aspect-ratio pores and tend to produce isotropic structures [2,3].

Freeze casting is a processing technique that is rapidly gaining interest due to its capacity to provide directionally aligned pores [4–7]. In freeze casting, pores are generated via the solidification of the liquid phase within a suspension of powdered solids, or alternatively, as will be treated here, the freezing of a solvent in a solution containing polymeric ceramic precursors. The frozen solvent acts as a sacrificial template and is consequently sublimated to create pores. Hence, directionality of the pore structure can be attributed to the thermal gradient applied from a cold surface. However since freeze casting is often performed by simply pouring a solution into a mold resting on a cold surface, random nucleation of crystals occurs at the base of the sample [8]. Although porous structures generated in this manner have indeed shown directionality, crystals growing at oblique angles that produce misaligned pores are also observed. For example, in water-based systems with lamellar crystals, numerous pore domains and boundaries are present since nucleation of certain ice crystals result in off-axis growth with respect to the thermal gradient [9]. These misalignments can reduce the homogeneity and directionality of the pore structure, effectively degrading its performance [10–12].

While many studies on freeze casting have explored the effects of various processing conditions such as solvent choice, particle size, and freezing front velocity on the pore structure, only a few studies have considered to control the process of nucleation and grain formation of solvent crystals. Recently, Bai et al. have shown that lamellar structures can be aligned by creating dual temperature gradients during solidification [13]. Munch et al. have also demonstrated the use of various patterned surfaces to manipulate the growth of ice crystals [14]. Although these methods have shown improvements in pore alignment, we take a different approach to the nucleation problem.

Here, a classic grain selection process is applied to freeze casting to achieve increased alignment of dendritic pores. Grain selection is a technique often used in metals processing where single crystal components are required. For example, Ni-superalloy turbine blades which require creep resistance at high temperatures are often produced using a spiral grain selector, also known as a pigtail [15,16]. In this work, instead of pouring the solution directly onto a cold surface, a 3D-printed template was placed between the casting mold and the cold surface to serve as a grain selector. This template decreases the number of off-axis solvent crystals and effectively increases the alignment of pores. Image analysis and permeability measurements were used to quantify the effectiveness of each template.

While freeze casting is often performed with suspensions of ceramic particles, preceramic polymer solutions can also be used to produce various porous ceramics [7,17]. In this study, polymer solutions were prepared by dissolving polymethylsiloxane (Silres® MK Powder, Wacker Chemie, CH₃-SiO_{1.5}, Munich, Germany) with cyclohexane (m.p. = 6°C, Sigma-Aldrich, St. Louis, USA). A cross-linking agent (Geniosil® GF 91, Wacker Chemie, Munich, Germany) was then added at 1 wt.% of the solution. The polymer solution was degassed prior to freezing to remove any air bubbles that may generate unwanted pores.

The freeze casting setup consists of a PID (proportional-integral-derivative) controlled thermoelectric device which sits on a heat sink cooled by refrigerated silicone oil. The polymer solution is poured into a cylindrical glass mold resting either on the thermoelectric or a designated template. In order to ensure comparable pore structures throughout the experiment, samples must undergo solidification at similar freezing front velocities [18–20]. For each sample, the PID controller was adjusted to specific temperature profiles, which resulted in a constant freezing front velocity of 5 µm/s. The freezing front velocity was easily observed and measured by camera since the polymer solution is optically transparent, but turns opaque when frozen. Following complete solidification, the sample is freeze-dried until all solvent is removed. The remaining porous polymeric structure is then heated in a flowing argon atmosphere at 2°C/min up to 1100°C and held for 4 hours to obtain an amorphous silicon oxycarbide (SiOC) ceramic. Each sample was sectioned and imaged at a height of 3mm from the base.

All samples freeze cast in this study were prepared with 20 wt.% of polysiloxane in cyclohexane which resulted in porosities of 67 to 74 vol.% after pyrolysis as determined by the Archimedes method (Table 1). Fig. 1 shows the typical dendritic pore structure obtained from this cyclohexane system. The transverse view in Fig. 1a shows the primary dendrites while the longitudinal view in Fig. 1b shows the secondary dendrites. These features produce a bimodal pore size distribution as characterized by mercury intrusion porosimetry, with pore diameters of roughly 35 and 25 μm respectively. Additionally, a lower magnification image (Fig. 1c) shows a representative structure of the freeze cast samples on a larger scale. While many pores align upward according to the temperature gradient (area 1), there are also pore domains which grow off-axis (area 2), and boundaries between each domain (area 3). To improve the pore alignment, a grain selection template is printed using a 3D printer (Autodesk Ember, San Rafael, CA, USA). Fig. 2 shows an example of a CAD drawing used to print a template. Each of the templates contained a hollow column located in the center acting as the grain selector. A total of three different templates with varying heights (h), hole diameters (d), and aspect ratios (AR) were used in this study. Template 1 is the shortest ($h = 5\text{ mm}$, $d = 1.5\text{ mm}$, $AR = 3.33$), Template 2 is taller ($h = 10\text{ mm}$, $d = 1.5\text{ mm}$, $AR = 6.67$), and Template 3 has a reduced hole diameter ($h = 10\text{ mm}$, $d = 0.5\text{ mm}$, $AR = 20$). The templates were designed as open sandwich structures to create sufficient thermal insulation to prevent nucleation from occurring anywhere besides the bottom of the designated hole. Consequently, this insulation also caused thermal conduction to be limited to just the 0.5 or 1.5 mm diameter column, severely limiting the cooling capacity, and hence a relatively low freezing front velocity of 5 $\mu\text{m/s}$ was used. In addition to the templated samples, a traditional control sample freeze cast directly on the cold surface was also analyzed for comparison.

Fig. 3 shows the evolution of the pore structure with respect to the different templates used. Images shown here were taken at very low magnifications to ensure that the image is representative of the whole sample and not biased toward a small and specific area. While this might present a challenge to identify individual pores, pores that are directly aligned with the freezing axis can be detected as dark spots. Fig. 3a shows that the control sample cast without a template contains very few areas with pores which are aligned directly parallel with the

temperature gradient. The majority of the area is composed of pore domains which are aligned slightly off-axis, and therefore are difficult to see when looking at a direct transverse cross-section. Since so many cyclohexane crystals have been allowed to nucleate on the cold surface, it is understandable that numerous solvent crystals have grown in this manner. However, Fig. 3b shows that once Template 1 is used and a grain selection process occurs, nuclei are forced to grow in a very constrained area and significant alignment is seen. Numerous large domains with pores highly aligned to the freezing direction are observed. Fig. 3c shows that alignment improves further when Template 2 is used and the height is increased from 5 mm to 10 mm. In this case, the increased length allows for more off-axis cyclohexane grains to be eliminated throughout the height of the template, resulting in even larger and more aligned pores. At this point, domains with aligned pores span several millimeters and cover most of the sample, leaving only a few grains growing off-axis. Lastly, the improving trend continues in Fig. 3d when the diameter of the column is reduced to 0.5 mm with Template 3. Here, we produce a sample with no distinguishable solvent crystals that have grown off-axis, resulting in fully aligned pores along the temperature gradient. The reduced diameter of the column proves to effectively reduce the amount of nucleation sites, enhancing the grain selection process along the height of the column. Despite this highly ordered pore structure, the cyclohexane did not seem to grow as a single crystal and boundaries are still present, producing the various pore domains seen in Fig. 3d. These boundaries can be attributed to low-angle domain boundaries or neighboring cyclohexane crystals that are rotated with respect to one another.

The increase in pore alignment from Fig. 3a to Fig. 3d may give an impression that the pore fraction has increased incrementally from one template to another, however this is not the case. As mentioned earlier, all samples were produced with the same polymer concentration and therefore have similar porosities. This illusion is simply a product of the pores being increasingly visible to the transverse cross-section as they become more aligned to the temperature gradient. Also, it is noteworthy that an additional sample was made with a template where no air insulation between the top and bottom surfaces was incorporated. The template is merely a solid polymeric block 10 mm tall, with a hollow column of 1.5 mm in diameter at the center. The resulting pore structure was largely identical to the control sample

(Fig. 3a) with mostly off-axis pore domains. Presumably, heat was conducted through the entire surface of the template rather than just the column, allowing nucleation to occur throughout the base of the sample as it did with the control scenario. This proves that a sufficient amount of insulation is required between the base of the sample and the cold plate in order to confine nucleation exclusively to the column area. While acrylate polymers like the one used in this study are generally good insulators, their thermal conductivity is still roughly an order of magnitude greater than that of air [21].

Image analysis was used to quantify the amount of change in pore alignment attributed to each template. Each image from Fig. 3 is segmented into the three separate types of domains mentioned in Fig. 1c; (i) domains parallel to the freezing axis, (ii) domains off-axis to the freezing axis, and (iii) domain boundaries. Fig. 4 shows each type of domain color-coded as green, purple, and orange, respectively. Here, the evolution of the microstructure through the different templates becomes more evident as the percentage of off-axis domains (purple) gradually decrease and are replaced with aligned pores (green). While most domains are distinguishable and contain boundaries between them, certain areas contain crystals rotated by low angles that barely show any boundary and can be difficult to discern. The total percent area occupied by each type of domain is listed in Table 1. It can be seen that the largest increase in percent of on-axis area (from 13.9 to 92.6%) and decrease in off-axis area (from 65.7 to 0%) comes from the transition between the control sample to that of Template 3. However, the largest incremental increase from one condition to the next comes from the control sample to Template 1. In this case, the percent of on-axis area increased from 13.9 to 58.6% and the off-axis area decreased from 65.7 to 25.2%. This shows that the use of a grain selection template is very effective even if the template does not have the ideal dimensions.

As a complementary test of pore alignment, permeability of porous cylinders, 3 mm x 13 mm $\emptyset$, made under each condition, was evaluated by measuring the flow rate of deionized water at various pressure drops. The flow rate was measured with a digital scale while the pressure was supplied by a voltage-controlled gear pump. Permeability constants were calculated according to the Forchheimer equation:

$$\frac{\Delta P}{L} = \frac{\mu}{k_1} v + \frac{\rho}{k_2} v^2$$

where ΔP is the pressure drop, L is the length of the sample, μ and ρ are the viscosity and density of the flowing fluid respectively, v is the flow velocity, and k_1 and k_2 are the Darcian and non-Darcian permeability constants. The non-Darcian permeability constant describes the non-linear behavior which arises at high flow velocities usually associated with gas flow. Since a liquid was used in this case, a linear behavior was observed and the k_2 term was therefore eliminated. A value of 8.90×10^{-4} Pa-s was used for the viscosity of water at 25°C. Table 1 lists the measured k_1 values for samples made with each template. The flow properties behave as expected in concert with results from image analysis; permeability increases steadily as the pores became progressively more aligned along the freezing axis and fluid flow direction. The change in flow behavior from the control sample ($k_1 = 3.4 \times 10^{-12} \text{ m}^2$) to the Template 3 sample ($k_1 = 2.1 \times 10^{-11} \text{ m}^2$) is significant – a more than six-fold increase.

In summary, this study shows that the use of grain selecting templates allows for greater control the nucleation process in freeze casting, consequently improving pore alignment along the freezing axis. Three different types of 3D-printed templates with varying heights and column diameters were used and compared with a traditionally freeze cast control scenario. Templates with higher aspect ratio holes (from 3.33 to 20) proved to be more effective in eliminating off-axis crystal growth and significantly improved the directionality of the pores. Image analysis was used to quantify the changes in the pore structures and results showed that the percent of pore domains aligned parallel to the freezing axis increased from ~14 to ~93%. Additionally, results from water permeability measurements show substantial improvement in flow properties as pore domains become more aligned. These improvements in pore alignment due to the use of grain selection templates demonstrate that controlling solvent crystal nucleation is crucial in freeze casting and should be taken into more consideration when trying to produce anisotropic and directionally-aligned pore structures. Further studies should address the low thermal conduction and freezing front velocity associated with the use of templates, likely resolved through an optimization of template material and design. Given that the process relies on grain selection during nucleation and growth, we speculate that this method is applicable not only to freeze casting of solutions (shown here), but also to more traditional freeze casting of ceramic suspensions.

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Figure captions

Fig. 1. (a) Primary dendrites seen from the transverse view perpendicular to the freezing direction and (b) secondary dendrites seen from the longitudinal view parallel to the freezing. (c) Low magnification image of the transverse view shows that sample features are not as uniform on a larger scale, consisting of aligned porosity (area 1), off-axis porosity (area 2), and domain boundaries (area 3).

Fig. 2. Representative CAD drawing of a 3D-printed template used for grain selection. The open structure provides additional insulation between the top and bottom plates to prevent unwanted nucleation. The diameter of the column and height of the templates are as follows: Template 1 ($h = 5\text{ mm}$, $d = 1.5\text{ mm}$); Template 2 ($h = 10\text{ mm}$, $d = 1.5\text{ mm}$); Template 3 ($h = 10\text{ mm}$, $d = 0.5\text{ mm}$).

Fig. 3. Low magnification SEM images of pore structures from (a) the control sample, (b) Template 1, (c) Template 2, and (d) Template 3. Scale bars = 1 mm

Fig. 4. Segmented and colored SEM images (from Fig. 3) of pore structures from (a) the control sample, (b) Template 1, (c) Template 2, and (d) Template 3. Each color represents particular features in the pore structure; pores parallel to the freezing axis (green), off-axis pores (purple), and domain boundaries (orange). Scale bars = 1 mm

Table 1. Open porosity, percent area occupied by different types of domains, and permeability constants for samples processed under each condition. Area calculations were based on segmented areas shown in Fig. 4.

	Open porosity (%)	Percent area parallel to freezing direction	Percent area off-axis to freezing direction	Percent area of boundaries	Permeability constant (m ²)
Control	72	13.9	65.7	20.4	3.4×10^{-12}
Template 1	74	58.6	25.2	16.2	4.9×10^{-12}
Template 2	67	79.8	9.3	10.9	1.1×10^{-11}
Template 3	71	92.6	0	7.4	2.1×10^{-11}

Figure 1

Figure 2

Figure 3

Figure 4 (COLOR)

Poor pore alignment

Grain-selection
template

Improved pore alignment