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Review Article

Intrinsic and extrinsic control of freeze casting

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ARTICLE INFO

Article history:

Received 11 June 2018

Accepted 21 November 2018

Available online xxx

Keywords:

Freeze casting

Ice-templating

Property control

Material fabrication

ABSTRACT

Freeze casting is a versatile material fabrication process that is known for its ability to create porous scaffold structures from effectively any constituent material. One of its advantages is that a wide variety of alterations to the processing conditions can result in drastic changes to the final micro- and macro-structure of the freeze-cast scaffolds and, therefore, its properties. Here, the authors present a novel view on these numerous control methods, through the concept that each of these methods for controlling freeze casting can either be considered to be an intrinsic or extrinsic control method. Intrinsic control methods act within the freezing process by altering the characteristic repulsive and attractive forces that govern the interactions between the solid loading particles and approaching freezing front during freezing of the slurry. Extrinsic control methods act upon the freeze process through the application of additional forces or energies, often external to the freezing process. This new system of understanding control over freeze casting is presented so as to inspire new work on the advanced control of freeze-cast scaffolds, specific work into extrinsic control methods and the interactions between intrinsic and extrinsic control methods.

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<https://doi.org/10.1016/j.jmrt.2018.11.011>

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1. Introduction to freeze casting

Also referred to as ice-templating, the freeze casting process has been studied for the last 20 years for its potential to create hierarchically structured, porous materials. Given its ease of use and inexpensive setup and maintenance it has shown promise as an efficient method to fabricate high surface area, porous materials for biomedical [1,2], energy [3,4], and structural applications [5,6], amongst others. An asset to the procedure is its material independence, with reports on freeze-cast scaffolds based on a variety of ceramics [2,7–9], metals [10–14], polymers [15–20], and even natural diatoms [21]. Given this material freedom, a wide variety of other methods and practices have arisen that provide control over the final micro- and macro-structure of freeze-cast scaffolds and, therefore, their properties. However, understanding these methods of control in a holistic manner is yet to be fully explored by the scientific community.

The freeze-casting process consists of four essential steps. (1) A colloidal slurry of a solid loading (e.g., ceramic particles) and a liquid freezing agent (e.g., water) is mixed along with additional additives such as polymeric binders and dispersants, which facilitate the process (Fig. 1a). (2) The mixture is directionally frozen, during which the solidification of the freezing agent induces a freezing front of ice crystals that segregate the solid loading (Fig. 1b). (3) Once fully solidified and directly after freeze casting, the frozen ice is sublimed out to leave a green scaffold, whose stability is dependent upon the polymeric binder (Fig. 1c). (4) The green scaffold is sintered to form a final scaffold where the resultant porosity, which bears the rough dimensions of the ice crystals, is found in the locations where the ice crystals formed and progressed through the slurry during step (2) (Fig. 1d). Of note, the sintering process, though not a specific focus of this review (as described below), will include the incineration of the organic binders that are present in the slurry, which will also alter the final material properties of the scaffold. In addition to these essential steps, many reports include a fifth, post-processing step (Fig. 1e). This can include processes such as the infiltration of a second polymeric [22], metallic [23,24] or glass [25] phase in order to form a two-phase composite or compaction of the scaffold to form a layered or brick-and-mortar structure [22,24,26]. Many of these post processing techniques result in increased mechanical properties that are in excess of a simple mixture of their constituents [22,25,27]. While these post-processing techniques have provided impressive results, the true control of the freeze casting process itself is a result of the fundamental freezing step (Fig. 1b), as this is where scaffold porosity and properties are initially developed. It is this essential process that will be the focus of this review.

A common freeze casting device consists of four main components: (1) a cold source (often in the form of a liquid nitrogen bath) that provides the sink with which to induce directional freezing, (2) a cold finger (most often a copper rod) that connects the cold source to the slurry, (3) a mold that holds the slurry in its liquid form (most often made of a polymer or other material with a low thermal conductivity so as to ensure directional freezing), and (4) a band heater or other method of temperature control that allows for some manner of control

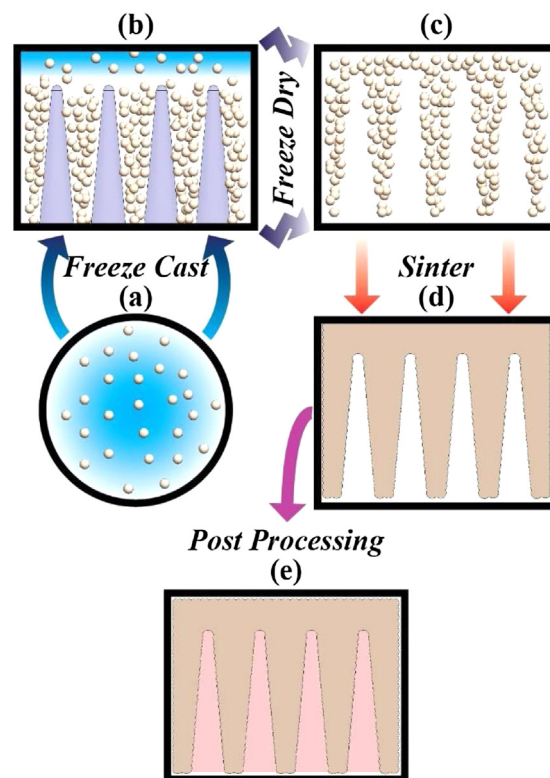


Fig. 1 – Diagram of the freeze-casting process, which occurs in four distinct steps. (a) A liquid slurry is mixed with a solid loading and slurry additives (e.g., binders and dispersants); (b) the slurry is directionally frozen in the characteristic freeze-casting step; (c) the freezing agent is sublimated through freeze drying, resulting in a green body; (d) the green body is sintered; (e) an additional fifth step can be added to the process where the sintered body is post-processed (e.g., infiltrated, mechanical loaded). This review is specifically focused on processes that occur during the freezing step (b).

over the temperature of the cold finger and, by extension, provides control over the freezing rate. A variety of alterations to this process have been demonstrated including active flow of liquid nitrogen over the cold finger [28], the use of multiple cold fingers and cold sources [7], and the use of thermally conductive molds to alter the freezing direction [29,30], to name a few. It is important to note that, for the proceeding discussion of control over freeze casting, while the freezing occurs at low temperatures, the overall freeze-casting device does not need to operate in any kind of globally (with respect to the freeze-casting process) controlled environment (e.g., high/low pressure or high/low temperature). Therefore, it is relatively easy to introduce additional devices or include a variety of chemical constituents in the process.

As there is no accepted standard of processing conditions (e.g., solid loading concentration, polymeric binder and dispersant use/variety) for the freeze-casting process, any discussion of the effect of isolated variables must be referenced to some baseline. As a result, throughout this document reference will be made to a “baseline” freeze-cast scaffold. Each of

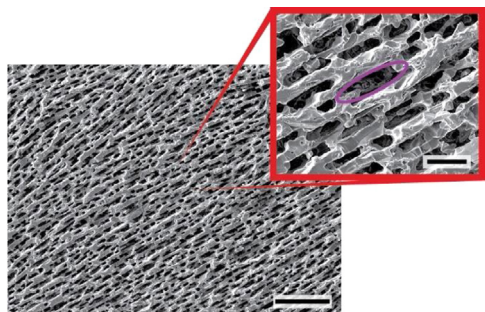


Fig. 2 – A cross-section of a baseline freeze-cast scaffold where the lighter contrast displays the ceramic walls and the darker contrast displays the porosity that is the result of the dendritic ice crystal growth. Inset displays the roughly elliptical porosity. Scale bars: 100 μm , inset: 20 μm . The image displays a cross-section that is perpendicular to the ice-growth direction.

the control methods described here drastically alter the structure of the freeze-cast scaffold from this baseline. The baseline scaffold described here (imaged in Fig. 2) is one that was frozen using a simple ceramic solid loading (hydroxyapatite in the case of the imaged scaffold) and pure distilled water freezing agent. These processing conditions produce a scaffold whose microstructure features aligned lamellar porosity, with an elliptical cross-sectional whose area is $\sim 500\text{--}1000\mu\text{m}^2$, and associated lamellar walls that are connected with mineral bridges (features that extend between the lamellar walls, but are generally of the same composition as the lamellar walls themselves). To fabricate such a scaffold, an aqueous slurry consisting of 15 vol.% ceramic particles (200–500 nm diameter) was mixed with 1 wt.% each polyethylene glycol (10,000 g mol^{-1}), polyvinyl alcohol (100,000 g mol^{-1}) binders and anionic dispersant. It was frozen at a constant cooling rate of 10 K min^{-1} , then freeze dried, and sintered. These particular scaffold processing parameters were chosen by the authors as they are, to our knowledge, close to what the majority of the freeze casting community would consider the simplest and most basic (consisting only of a ceramic solid load, a water freezing agent, and basic binders and dispersants).

2. Understanding control of the freeze-cast structure

A critical parameter to comprehend the current theoretical understanding of the freeze-casting process, and to a larger extent colloidal solidification processes, is the thermodynamic free energy of the system [31,32]. Consider the system, diagrammed in Fig. 3 [31], where the freezing front is approaching a single solid particle that is spherical in shape. For that particle to be rejected (i.e., pushed away from the freezing front as opposed to trapped inside it) the free energy of the system, $\Delta\gamma_0$, must be positive:

$$\Delta\gamma_0 = \gamma_{ps} - (\gamma_{pl} + \gamma_{sl}) > 0 \quad (1)$$

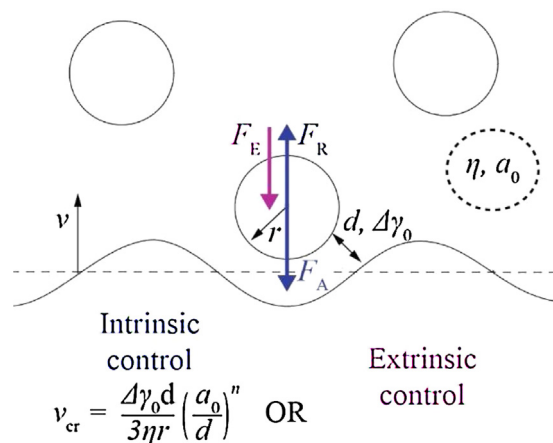


Fig. 3 – Current freeze casting theory that considers the process to be governed by an energy balance between the progressing freezing front and a solid loading particle. This can result in an equation for the critical velocity, v_{cr} , below which the particle will be rejected, thus becoming part of the lamellar walls that are characteristic of freeze casting. The authors propose that this equation can be applied for intrinsic control, while extrinsic control will generally act outside of this process (e.g., an external force such as F_E in the figure).

where $\Delta\gamma_0$ is dependent on the interfacial energies of the particle and solid ice phase, γ_{ps} , the particle and the unfrozen liquid phase, γ_{pl} , and the solid and liquid phases, γ_{sl} . As shown in Eq. (1), for a particle to be trapped, the free energy of the interface created during entrapment between the particle and the solid ice, γ_{ps} , must be larger than the sum of the energies that are lost to the system during entrapment ($\gamma_{pl} + \gamma_{sl}$), thus moving to a lower energy state [31]. This free energy is a critical component in the simplified balance of the system where the particle in the liquid phase will experience both repulsive, F_R , and attractive, F_A , forces to the freezing front due to van der Waals interactions at the liquid-solid interface and viscous drag, respectively [31]:

$$F_R = 2\pi r \Delta\gamma_0 \left(\frac{a_0}{d}\right)^n \quad (2)$$

$$F_A = \frac{6\pi\eta v r^2}{d} \quad (3)$$

where r is the radius of the solid particle, a_0 is the mean distance between molecules in the liquid phase, d is the thickness of the liquid layer between the solid-liquid interface and the particle (i.e., the distance between the ice front and the particle), n is an empirical factor that is a correction to the repulsive forces acting on the particle and generally ranges from 1 to 4 [31,33], and η is the dynamic viscosity of the liquid. Equating F_R and F_A and solving for the ice front velocity, v , results in an expression for the critical freezing front velocity, v_{cr} , at which a particle will be trapped:

$$v_{cr} = \frac{\Delta\gamma_0 d}{3\eta r} \left(\frac{a_0}{d}\right)^n \quad (4)$$

Therefore, for $v > v_{cr}$, particles will generally be entrapped by the solid phase, creating mineral bridges within the resultant porosity and for $v < v_{cr}$, particles will generally be rejected and become part of the lamellar walls of the final freeze-cast scaffold. This force balance, born from the original F_R and F_A terms, contains terms that describe the nature of the liquid phase (η , a_0), the solid particles (r), and the interactions between the particles and the approaching freezing front (v_{cr} , d , n , $\Delta\gamma_0$). This current force balance can describe interactions that occur within the freezing. However, another option for control are any additional or external forces or energies that act on the particle, ice growth or system, where its specific form will depend on the nature of the applied force or energy.

One important assumption that is made here is that the focus is placed only on the interactions between a single particle and the approaching freezing front. In reality, there are numerous particles that interact between each other within the slurry. Peppin et al. [34], Rempel and Worster [35], and Saint-Michel et al. [36] have each provided insights into these more complex systems where an additional force is exerted on a particle interacting with the freezing front (as is described in Eqs. (2) and (3)) by the mass of particles (or particle layer [36]) that sit within the liquid slurry, above the particle in question. This force results from the viscous stresses and pressure drop that result from the fluid flow that interacts with the particle layer as the freezing front moves through the slurry [36].

When considering control over the final materials created by freeze casting, this theoretical force balance offers a nexus to understand the variety of methods that have been described as well as those involved in future work. With this as a guide, we propose that control of freeze casting can be considered to be by intrinsic or extrinsic means as described below:

- **Intrinsic:** control that acts within the freezing process through modification of the slurry constituents and/or the freezing rate, thus altering the repulsive and attractive forces that a particle experiences when interacting with the freezing front as described by F_R and F_A balance in Eq. (4). In addition, some of these methods will impact the morphology of the ice crystals formed during freezing, which may be their dominant method of altering the final freeze-cast scaffold. These methods of control tend to alter the pore size and shape, but apply to the entire slurry and therefore can lack the ability to affect complex control over the microstructure.
- **Extrinsic:** control that acts upon the freezing process through the application of exterior/additional forces or energies that transcend the force balance described in Eq. (4). These methods of control tend to alter the entire microstructure, allowing for different levels of control in different areas, while generally struggling to alter the individual pore size and shape.

There are a multitude of currently reported techniques of each of these methods of control, notable examples of which will be described in more detail in this review. Two common methods of control over freeze casting and freeze-cast materials will not be discussed here: alterations to the sintering procedure and post processing of the material (e.g., infiltration). Neither of these are primarily focused on the critical

freeze-casting step and therefore will be omitted. Of note, Munch et al. [37], Porter et al. [38], Gutierrez and Ferrer [39], Li et al. [40], Liu et al. [41], Qian and Zhang [42], Scotti and Dunand [43], and Deville [44,45] (along with a published book authored by Deville [46]) provide excellent reviews on the freeze-casting process from a variety of perspectives that should be considered to augment the information presented here.

3. Intrinsic control of freeze casting

Intrinsic freeze casting mechanisms include controlling the freezing rate (Fig. 4a) [7], the use of varying freezing agents (Fig. 4b) [47], additives to the slurry (Fig. 4c) [48], and altering the particle size of the solid loading (Fig. 4d) [49]. Of note, the variation of the freezing agent and the addition of additives could be considered interchangeable. In many cases, this distinction can be made by grouping changes in chemistry that react to form new compounds (as determined by a phase diagram) as variations of the freezing agent while changes in chemistry that do not react in solution as additives. However, in lieu of such information (e.g., for complex chemistries), when discussing alterations to the liquid freezing agent with the intention of modifying the ice crystal structure or properties the authors provide a general guideline. Based on the current experiments provided in the literature and their own empirical experience, the addition of ≤ 30 vol.% of a second phase (e.g., an additive such as a monofunctional alcohol) or chemistry is considered here to be an additive, while > 30 vol.% is considered to be a different freezing agent. As described below, these additives and freezing agents generally operate by altering the geometry of the ice crystals that form during freeze casting, therefore resulting in different pore geometries. As shown in Fig. 4, in each case, these intrinsic control methods are able to alter the structure of the pores in a uniform way across the entire freeze-cast scaffold.

3.1. Freezing rate

As demonstrated by Eq. (4), the freezing rate has a critical effect on the physics of freeze casting [31]. In addition, the freezing rate will alter the radius of curvature of the ice crystal during freezing. This has been empirically demonstrated on a number of occasions [7,37,44,50–54], where an increase in the ice front velocity, v , can be inversely related to the ice crystal size, or the pore size, w , in the final freeze cast scaffold [31].

$$w \propto \frac{1}{v^n} \quad (5)$$

The freezing rate can be linked to a common phenomenon within freeze casting whereby the scaffold structure, located close to the copper cold finger, has a considerably finer pore structure [2,50,53]. This can be directly linked to the freezing rate that experiences an exponential decay (with respect to time starting with the beginning of the freeze-casting process) from its initial moments to a steady-state rate [50,51,55]. These changes in the freezing rate, which has been extensively studied by Deville et al. [50,56], can be linked to associated changes in the ice crystal structure. In this, a rapid freezing rate results

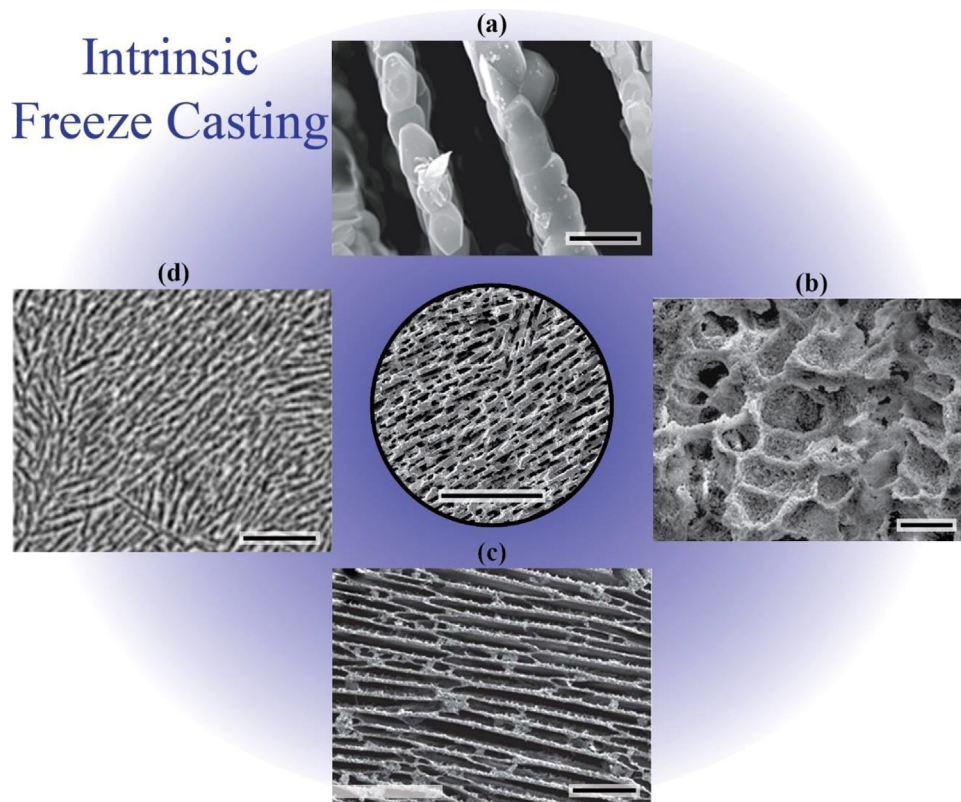


Fig. 4 – Examples of intrinsic freeze casting. (a) Thin lamellar walls induced by a high cooling rate; (b) cellular porosity through the use of camphene as a freezing agent; (c) enlarged porosity through the use of isopropanol as a slurry additive; (d) a structure with smaller interlamellar spacing due to the use of a large solid loading particle size. For reference, the central image is of a baseline scaffold. Scale bars: (a) 4 μm , (b) 20 μm , (c) 200 μm , (d) 150 μm , and center: 100 μm . All images display cross-sections that are perpendicular to the ice-growth direction. Images adapted with permission from: (a) [7], (b) [47], (c) [48], and (d) [49].

in a randomly oriented structure and a slower, steady-state freezing rate results in a structure that is aligned with the ice-growth direction. Of note, this steady-state rate produces the lamellar walls and porosity that is most often desired in freeze-cast scaffolds.

Freezing-rate control over the pore size has not been shown to alter the total porosity of freeze-cast scaffolds [52]. Therefore, to conserve mass this increase in the pore size can be directly related to an increase in the lamellar wall thickness of the scaffolds and a reduction in their quantity, which generally results in a decrease in the scaffold's mechanical properties [37,57]. As will be discussed below, many other intrinsic methods of freeze-casting control are effective due to their ability to decrease the freezing rate, including the use of ethanol as a slurry additive [37] and increasing the solid loading content [53].

3.2. Freezing agent

When a non-water-based freezing agent is employed in freeze casting the dynamics of solidification are significantly altered. This tends to manifest itself in a very different structure of ice growth, which in turn results in different pore geometries; with its effect on the force balance described in Eq. (4) acting

in a secondary role as to the impact on the final freeze-cast scaffold. These freezing agents can drastically alter the surface energies (as described in Eq. (1)), or fluid dynamics (η and α_0 in Eq. (4)) that govern freeze casting, resulting in significant changes in the freeze-cast scaffolds. The use of freezing agents is limited by the liquid's solidification structure as not all types of ice growth are capable of rejecting the solid loading particles in a way that will result in a final, porous freeze-cast scaffold. Most liquids will solidify into either a dendritic or faceted structure [31], with dendrites being necessary in the critical freezing step of freeze casting (Fig. 1b) to create open porosity that is generally desired. The freezing agent's solidified structure can be predicted using an α -value [28,58,59]:

$$\alpha = \frac{h_E \xi}{RT_E} \quad (6)$$

where h_E is the latent heat, ξ is an empirical factor that depends on the crystallography of the interface, R is the gas constant, and T_E is the equilibrium temperature between the solid and liquid phases. ξ generally ranges from 0.5 to 1 when the close-packed plane of the crystal makes up the interface and decreases with higher index planes, however it will vary in empirical experiments and therefore is often left as a variable when describing the α -value. Liquids that have $\alpha < 1$ will

generally freeze with a dendritic structure [28]. Of note, pure water has a value of approximately $\alpha = 2.6\xi$ [59], demonstrating that, even in this common case, the crystal orientation can have a significant effect on the nature of the ice growth, and therefore on the freeze-cast scaffold.

Perhaps the most commonly used non-water-based freezing agent is camphene [47,58–70]. Camphene ($C_{10}H_{16}$, $\alpha = 1.1\xi$ [59]) and camphene-based solutions are of particular interest given their high solidification temperatures (44–48 °C for pure camphene [70]) that allow for slurries to be frozen at room temperature. Due to the dendritic shape of freezing camphene, the resultant freeze-cast scaffolds have a cellular porosity structure with pores that are more circular than elliptical (Fig. 4b). Other freezing agents include cyclohexane, which results in a similar, cellular structure [71,72], and tert-butyl alcohol (TBA), which can be frozen at room temperature (with a freezing point of $\sim 25^\circ\text{C}$) with the use of acryl-amide as a polymerization agent [71,73], or at lower temperatures when applied without a polymerization agent [71]. TBA crystals take on a prismatic form in contrast to the dendrites of ice, resulting in a freeze-cast scaffold with polygonal pores [71,73].

3.3. Slurry additives

Likely the most broadly researched area of freeze-casting control; slurry additives have been demonstrated to significantly impact the microstructure of the freeze-cast scaffolds, often while requiring only small quantities of additives. These most often operate with two distinct mechanisms: (1) changes in the slurry viscosity or pH, which result in associated changes in the ice-growth velocity and/or a change in the ice crystal morphology, thus increasing or decreasing the pore size and (2) the introduction of new chemical structures in addition to the ice dendrites.

In many cases, the effects of slurry additives can be traced to changes in viscosity or pH that directly alter the freeze rate of the slurry. A number of authors have specifically connected changes in viscosity, induced by the addition of slurry additives, to changes in the pore size. This has been shown with a variety of polymeric additives including high molecular weight PVA or PEG [48,74,75], glycerol [76], gelatin [77], and sucrose [37]. Similarly, the pH has been demonstrated to alter the pore size with additives such as citric acid [37], hydrochloric acid and sodium hydroxide [48], and acetic acid [78]. These can impact the ice crystal morphology and/or be directly linked to Eq. (4), where the freezing agent's dynamic viscosity, η (which is related to both the pH [79] and, naturally, the viscosity) is inversely related to the freezing front velocity, v . However, in a number of reports [48,74], it has been shown that the relationship between pore size and viscosity displays a concave parabolic trend. Porter et al. [48] proposed that this was due to the interplay between two physics: the freezing front velocity, v , and the amount of constitutional supercooling. Constitutional supercooling occurs when the applied thermal gradient in the slurry (G^L) is less than the equilibrium thermodynamic temperature, as described by the following equation (7) [80]:

$$G^L < \frac{v}{D}(T^{\text{liq}} - T^{\text{sol}}) \quad (7)$$

where D is the mass diffusivity of the liquid and T^{liq} and T^{sol} are the equilibrium liquidus and solidus temperatures, respectively. The mass diffusivity is inversely related to the viscosity of a liquid through the Stokes–Einstein equation [81]. Therefore, as the viscosity increases, so too does the amount of constitutional supercooling, which will increase the freezing-front velocity [48] and therefore counteract the decrease in the freezing-front velocity that is associated with a more viscous slurry.

Another common route to alter the structure of freeze-cast scaffolds with slurry additives is to induce the formation of new, but dispersed chemical structures. The nature of these newly formed chemical structures can drastically alter the pore structure in the freeze-cast scaffold. The use of monofunctional alcohols such as ethanol (C_2H_5OH), propanol (C_3H_7OH), and butanol (C_4H_9OH) have been shown to induce the formation of clathrate hydrates [5,27,48], which are enlarged, non-stoichiometric structures where a captive guest molecule (in this case the alcohol) is enclosed in a hydrogen-bonded lattice (in this case water) [82]. These structures have been shown to result in drastically increased pore sizes (Fig. 4c) [5,27,48], often orders of magnitude larger than those observed in a baseline freeze-cast scaffold. Another notable example of inducing new chemical structures is the use of natural ice-structuring proteins and antifreezes [45]. Natural antifreeze proteins, many of which naturally occur in organisms such as polar fish and frogs, have been shown to significantly alter the structure of ice crystals [83–85]. Inspired by these ice-structuring proteins, a number of reports have discussed the use of zirconium acetate (ZrAc) as an additive with the ability to modify the structure of growing ice and affect freeze-cast scaffolds [86,87]. Deville et al. [86] proposed that ZrAc in solution will adopt a hydroxyl-bridged polymer structure that binds to the surface of ice crystals, slowing their growth and modifying their structure, thus resulting in hexagonal pores within the freeze-cast scaffold.

3.4. Solid loading structure, concentration, and chemistry

While the first three methods of intrinsic control described here all focus on the freezing agent (both in its solid and liquid form), the solid loading can also play a strong role in the final structure of the freeze-cast scaffold. The properties of the solid loading, specifically the concentration [2,88–91], particle size [49,92], particle shape [93,94], and particle chemistry [38,95,96] are known to affect the microstructure of the freeze-cast scaffold.

The particle concentration has an intuitive effect on the freeze-cast scaffold microstructure, where the total porosity of the scaffold is directly related to the initial concentration [2,88–91]. The limits of this method of control are generally bound as lower concentrations can result in mechanically unstable scaffolds (either after freeze drying or sintering), while higher concentrations can result in scaffolds that lack the open-cell and lamellar porosity that is generally desired in freeze-cast scaffolds. While these bounds vary with a number of factors (e.g., the solid loading and freezing agent chemistry, the sintering procedure, the freezing rate), the authors provide

a general guide that slurries with solid loading concentrations >45 vol.% and <5 vol.% will often produce unfavorable results in the freeze-cast scaffolds.

The effects of particle size can be directly related to the thermodynamics that drive freeze casting. Conceptually, larger particles have more surface area and (ignoring the particle chemistry and tribology) a higher surface energy when suspended in the liquid phase, γ_{pl} , which can be related to the particle's interaction with the freezing front as shown in Eqs. (1) and (4). Therefore, as described in Eq. (1), greater energy is required to create an environment favorable for the particles to be rejected by the freezing front, resulting in the ideal freeze-cast structure. This has been demonstrated in a number of reports that compare relatively larger and smaller particles. When considering a particle to be individually interacting with the freezing front a larger particle will have a larger surface and therefore surface energy than a smaller particle. Therefore, a larger particle will have a lower freezing velocity (as described in Eq. (4)), a higher degree of constitutional supercooling, and larger pores in a resultant freeze-cast scaffold [49,92]. Of note, if particles become too large and are therefore no longer colloidal in the slurry, the force of gravity would need to be considered in the force balance described in Eq. (4). However, these cases are generally not successful at creating freeze-cast scaffolds, as the particles will tend to settle out of solution prior to freezing. Deville et al. [56] have also shown that the particle size can alter the ice growth by dictating the transition from metastable to unstable growth of the ice front (specifically with larger particles driving toward metastable growth). In addition, it has been proposed that particles can also act as nucleation sites for ice crystals during freezing [49]. When considering the same samples of equal mass, smaller particles, which will have a higher surface area when compared to larger particles, offer more nucleation sites for ice growth and faster overall freezing. Beyond the pore size, smaller particles have also demonstrated the ability to provide greater resolution or detail as smaller particles can better conform to the features of the ice dendrites [8].

Effects of the particle shape is an area that could benefit from additional research. There have been a few reports on the use of high aspect ratio platelets in freeze casting [93,94,97,98]. These have demonstrated that the platelets can experience shear forces from the growing ice dendrites that result in their alignment and self-assembly [93]. In addition, it has been shown that platelets can act as reinforcing grains within the freeze-cast scaffold, thus increasing the strength by redirecting crack growth [97,98]. However, given that the existing physics on freeze casting focuses on particles that are, in theory, perfectly spherical (as described in Eq. (4)), there is ample room to better understand the effects of particle shape on the structure and properties of freeze-cast scaffolds.

One of the specific advantages of freeze casting is its ability to be applied to effectively any particle chemistry [8]. While there are few material particles that cannot be freeze cast, the particle's chemistry does still provide some control over the final structure, even when, as is done in this review, the sintering procedure is ignored. This can be easily observed in the energy balance described in Eq. (1) [31,32] where the surface energy (a property that depends on the particle's chemistry) between the particle and its surroundings (both the liquid

and solid phase) is critical to the interaction between particles and the approaching freezing front. When considering multiple particles, the viscous forces of the particle mass above the freezing front will be determined, in part, by the viscous flow of fluid over the particles' surfaces [36]. Functionally, the freezing point of the slurry will be partially determined by the particle chemistry, which in turn will alter the freezing rate at the initial points of freezing [34]. In addition, certain particle chemistries will result in specific functionalities such as chain formation due to ferrimagnetic behavior in Fe_3O_4 [38] particles or micelle formation with block copolymers particles [95,96], amongst others. The thermal conductivity of the particle will also alter the freezing dynamics of the slurry. Garvin and Udaykumar [99] (using a metal melt system, but describing physics that also apply to freeze casting) have demonstrated that the thermal conductivity of the particle (or, more specifically, the ratio of the thermal conductivity of the particle to the thermal conductivity of the liquid phase) alters both the drag force experienced by the particle and the morphology of the freezing front. Specifically, higher thermal conductivities relate to higher drag.

4. Extrinsic control of freeze casting

Extrinsic freeze-casting mechanisms include applications of mechanical templates (Fig. 5a) [100], external energized fields such as magnetic (Fig. 5b) [6] and electrical (Fig. 5c) [101] fields, and directional control of the freezing (Fig. 5d) [102]. These allow for complex control over either the macrostructure or the porosity of the freeze-cast scaffolds. This can be particularly useful when creating structures with hierarchical, gradient, or generally complex porosity at multiple length scales. Intrinsic control over freeze casting alters the pore structure or freeze-cast structure in a uniform way (i.e., any change made to the slurry or freezing dynamics tends to be made throughout the entire freeze-cast scaffold), thus generally limiting the pore structure to a single length scale. In contrast, extrinsic control demonstrates no such limitation, allowing for more complex structures to be fabricated.

4.1. Mechanical templates

Perhaps the simplest way to induce external forces is with the use of mechanical templates that physically block or redirect the growth of ice. This is most often implemented in the form of complex polymer structures. Given their low thermal conductivity, polymer structures will generally act as insulators and not nucleate ice growth themselves, only redirecting or blocking the ice growth from the freezing front. These templates are often, though not always, sacrificial. This can be easily facilitated by the sintering process where high temperatures can incinerate polymer templates while densifying the freeze-cast scaffold. This results in voids in place of the templates and provides an easy pathway to porosity on multiple length scales, which can be advantageous in many applications. For example, common application for this method of extrinsic control is to create materials that are mimetic of the complex structure of bone [100,103,104], where porosity at both the μm and mm length scales play critical

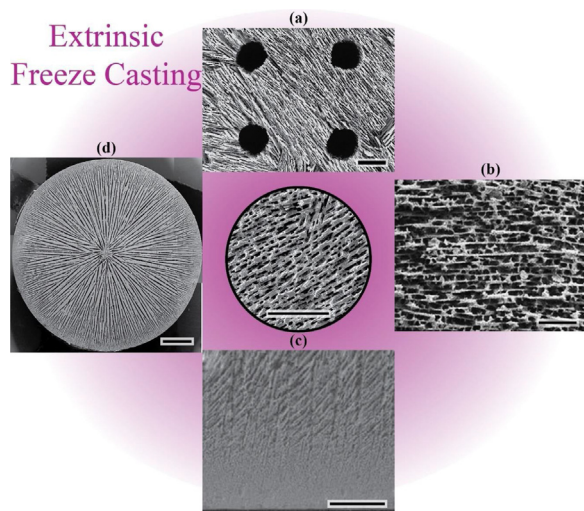


Fig. 5 – Examples of extrinsic freeze casting. (a) Macro-micro porosity caused by the use of a sacrificial mechanical template; (b) aligned porosity through the application of magnetic fields; (c) dense/porous bilayered porosity through the application of electric fields; (d) centrosymmetric porosity through radial cooling. For reference, the central image is of a baseline scaffold. Scale bars: (a) 500 μm , (b) 100 μm , (c) 200 μm , (d) 2 mm, and center: 100 μm . (a), (b), and (d) display cross-sections that are perpendicular to the ice-growth direction, while (c) displays a cross-section that is parallel to the ice-growth direction. Images adapted with permission from: (a) [100], (b) [6], (c) [101], and (d) [102].

roles in the strength and health of bone [105]. Two common varieties of sacrificial templates are large structures (often skeletons [100,103,106–108]) and smaller, dispersed particles [109].

Larger structures are generally implemented to alter the ice growth path, which can lead to a variety of complex microstructures in the freeze-cast scaffolds. Sponges (Fig. 6a) [107,108] and skeletons or wedges [100,103] (which will be discussed in more detail below as they alter the freezing direction) are often employed as placeholders that are then chemically dissolved or incinerated during sintering. These offer the ability to create truly hierarchical porosity on multiple length scales. In addition, given availability of additive manufacturing, it is possible to create user-defined geometries in these templates that translate to complex porosities in the freeze-cast scaffold.

An alternative method to employ mechanical templates to extrinsically control the structure of freeze-cast scaffolds is through the use of dispersed, sacrificial particles that are mixed with the slurry, freeze cast, then incinerated during sintering (Fig. 6c) [109,110]. These particles are generally made of polymers (e.g., polystyrene) to allow for easy removal by incineration. Their size and shape can directly dictate the final porosity of the freeze-cast scaffold. This has resulted in examples of templating particles that are both larger [109] and smaller [110] than the characteristic ice crystals.

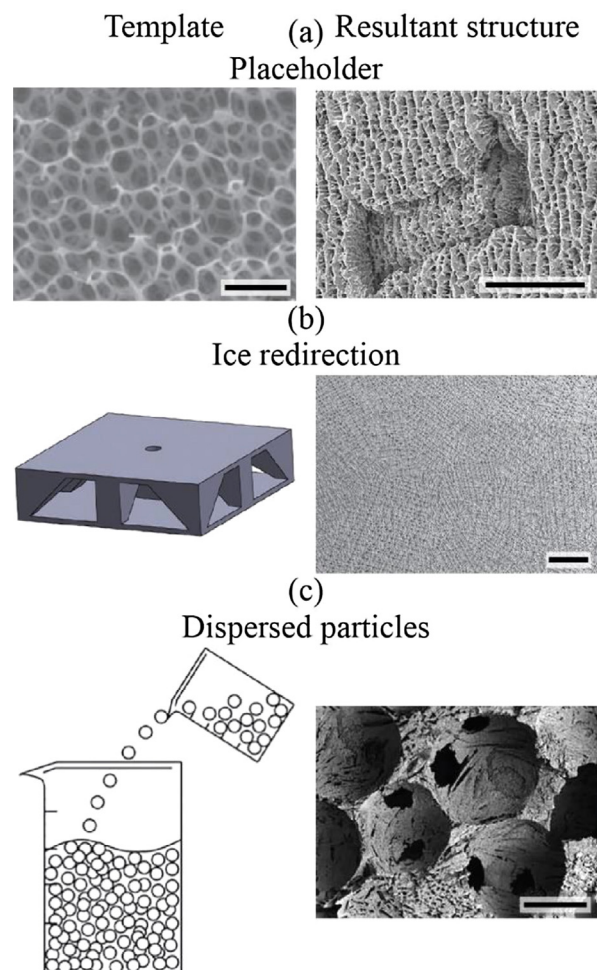


Fig. 6 – Examples of extrinsic control through the use of mechanical templates. (a) A polymer sponge that acts as a sacrificial placeholder in the slurry and results in additional porosity in the freeze-cast scaffold; (b) a grain selector that redirects the ice growth to produce a specific structural orientation in the freeze-cast scaffold; (c) sacrificial dispersed particles that are introduced to the slurry and result in distributed porosity in the freeze-cast scaffold. Scale bars: (a) left: 1 mm, right: 200 μm , (b) 1 mm, and (c) 2 mm. All images display cross-sections that are perpendicular to the ice-growth direction. Images adapted with permission from: (a) [108], (b) [106], and (c) [109].

4.2. External force fields

A number of reports have shown that dispersed or colloidal particles can be manipulated via electric field [111], magnetic field [112,113], and ultrasound waves [114,115]. Mimicking such techniques during the freezing process has led to highly controllable extrinsic methods to improve the mechanical and structural properties of freeze-cast scaffolds [94,116–118,6,119–121]. Of note, these methods of control, though described here as extrinsic, can often induce effects that can be considered both intrinsic and extrinsic. For example, the application of a magnetic field may both lead to chain

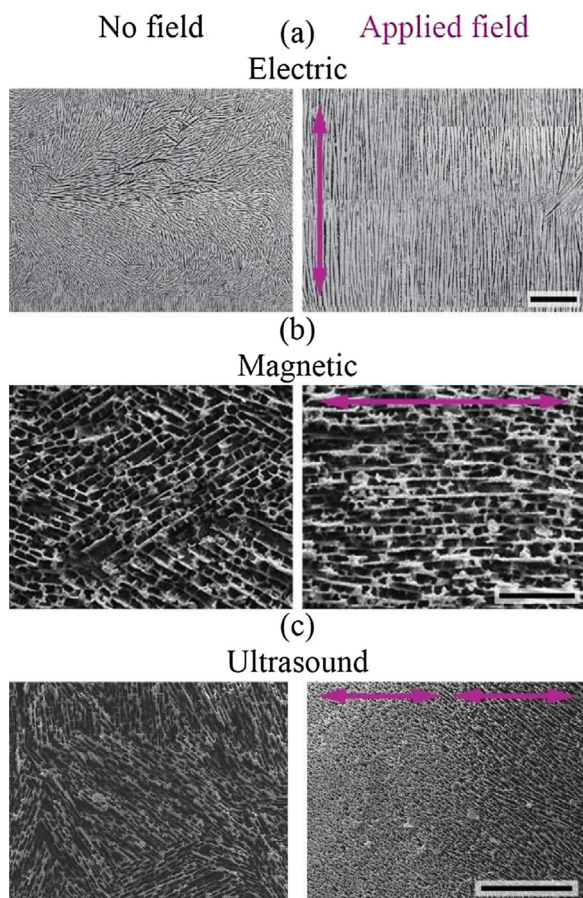


Fig. 7 – Examples of extrinsic control through the use of energized fields. Examples of applied (a) electric, (b) magnetic, and (c) ultrasound fields are shown with examples given of the freeze-cast scaffold with and without an applied field in each case. Purple arrows indicate the direction of the applied field. Scale bars: (a) 2 mm, (b) 100 μm , and (c) 400 μm . All images display cross-sections that are perpendicular to the ice-growth direction. Images adapted with permission from: (a) [116], (b) [6], and (c) [121].

formation of particles (thus creating additional forces between particles, which is considered intrinsic) and force the motion or rotation of individual particles (thus applying an external force directly onto the particle, which is considered extrinsic).

Electric fields up to 150 kV/m have been applied in the perpendicular to the ice growth direction while simultaneously freezing from three copper freezing surfaces of a cubic mold, as shown in Fig. 7a. Because water molecules have a permanent dipole moment, an applied electric field can alter the preferential orientation and nucleation of ice crystals, thus directing the overall direction of ice growth [116,122,123]. This phenomenon has been shown to align pore channels along the applied electric field increasing the ultimate compressive strength in that direction [116].

Using magnetic fields during freeze casting has shown to align particles and structures in freeze-cast scaffolds and, therefore, improve their mechanical properties. Depending

on the magnetic susceptibility of the particles used, varying magnetic field strengths can be used to manipulate the particles by either aligning them using a uniform magnetic field or positioning them using a magnetic gradient. Magnetic fields as high as 150 mT [117] and as low as 2.6 mT [120] have shown to improve the mechanical properties in the direction of the applied magnetic field. Predominantly, the magnetic field has been applied in the direction perpendicular to the ice-growth direction using permanent magnets resulting in higher mechanical properties (Fig. 7b) [94,117,118,6,119]. Spatial limitations hinder the ability of using permanent magnets to apply a uniform magnetic field parallel to the ice-growth direction, specifically due to the location of the cold finger. However, a Helmholtz coil was found to overcome this limitation and apply a uniform magnetic field and improve the mechanical characteristics parallel to the ice-growth direction [120].

Ultrasound waves created by a PZT ultrasound transducer with frequencies up to 936 kHz have been shown to create standing waves that induced areas of high and low particle concentrations during freeze casting (Fig. 7c). These standing waves result in local minima in pressure where particles are more likely to agglomerate [124]. The resulting freeze-cast scaffolds have high and low density regions having higher and lower material hardness, respectively [121]. Due to the cylindrical shape of the PZT transducer, these regions appear as rings, however this technique has been demonstrated to be able to create effectively any pattern [125]. Having these high and low density regions can lead to improved mechanical characteristics over homogenous scaffolds [121].

4.3. Freezing direction

There have been a number of reports on the use of multiple freezing fronts induced by multiple cold sources, resulting in multidirectional [116,126,53,127,104] and radial [128–130] alignment in freeze-cast scaffolds. When considering these, a simple method of organization is to determine the number of directions ice is grown from (i.e., temperature gradients), with baseline freeze casting having only one such direction of ice growth, as shown in Fig. 8a. In general, the addition of temperature gradients results in associated regions of aligned porosity in freeze-cast scaffolds.

Bidirectional experiments have been performed by freezing in a single direction from both the top and bottom of cylindrical scaffolds [126,53]. Additionally, a novel method to get lamellar walls aligned in a single direction was achieved by adding a PDMS wedge to the mold to create competing temperature gradients. As the ice crystals grow from a single bottom cold finger, the competing ice-growth directions create lamellar wall alignment (Fig. 8b) [127]. Similarly, when freezing in two [131] or three directions (i.e., from the bottom and two sides) of a cubic mold, the lamellar walls align into three distinct regions (Fig. 8c) [116]. Pot et al. [132] and Bai et al. [104,127] have demonstrated that the use of a PDMS wedge forces the freezing front to progress in a manner that results in highly aligned ice crystals. This results in freeze-cast scaffolds without the orientation domains that often appear due to initial nucleation and growth events, followed by the natural selection of grains during growth [46,51].

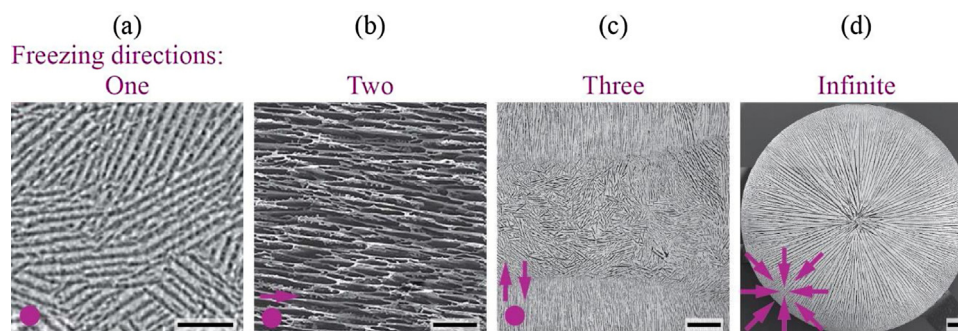


Fig. 8 – Examples of extrinsic control through changes in the freezing direction. Examples are given based on the number of different freezing directions applied with (a) one, (b) two, (c) three, and (d) effectively infinite directions. Purple arrows indicate the applied freezing directions with a circle representing freezing out of the plane. Scale bars: (a) 150 μm , (b) 200 μm , (c) 2 mm, and (d) 2 mm. All images display cross-sections that are perpendicular to the ice-growth direction. Images adapted with permission from: (a) [51], (b) [104], (c) [116], and (d) [129].

Further research demonstrated that increasing the slope of this wedge structure can provide more ordered freeze-cast scaffolds [127]. Naviroj et al. [106] (Fig. 6b) was similarly able to use a polymeric grain selector to induce highly ordered freeze-cast scaffolds that significantly improved their permeability. This was measured as measured by a 6-fold increase in the Darcian permeability constant of the freeze-cast scaffold.

Radial freeze casting (i.e., effectively infinite freezing directions) produces radially symmetric scaffolds as shown in Fig. 8d [129,133]. This results in the lamellar walls being radially aligned and an increase in the mechanical strength (including fracture toughness) in the radial direction [129]. Another notable result of radial freezing is the variable spacing between lamellar walls along the ice growth direction [130]. This can be linked to the ice front velocity, which greatly decreases or increases throughout the slurry due to the freezing front interface area increasing (when freezing from the center to the outside) or decreasing (when freezing from the outside to the center).

5. Potential of combined control methods

While this review has explicitly taken the position of examining each individual method of intrinsic and extrinsic control on its own, there is ample room to investigate their combinations and interactions. For example, Bouville et al. [25] recently reported on bioinspired ceramics created using a process that harnesses both platelet-shaped particles (an intrinsic method) and directional freezing (an extrinsic method). However, given the current state of the field where reports tend to focus on individual control methods, it is difficult to identify a significant number of current reports that specifically look to discern the interactions between methods of control on freeze casting. However, this may certainly offer an avenue for future research as the majority of control methods are applied in ways such that they would not inhibit the application of a second or third method of control. Perhaps of greatest interest would be the specific combinations of intrinsic and extrinsic control methods. As described here, these methods operate on the freezing process differently and therefore would likely be able

to exert control over the properties of the freeze-cast scaffold simultaneously, without diminishing each other. Specifically, as intrinsic control methods tend to alter the structure of the pore shape and size uniformly and extrinsic control methods tend to alter the microstructure overall, their combination could provide hierarchical control over the structure and properties of freeze-cast scaffolds.

6. Conclusions and future outlook

In summary, the freeze casting fabrication technique displays significant potential to benefit a wide variety of materials science and engineering applications, including biomedical implants with a porous structure to promote cell ingrowth and healing, high strength-low density structural composite materials, water filtration systems, and battery catalysts, to name a few. One of its primary advantages is the wide variety of methods that can be applied to drastically alter the properties (e.g., structural, mechanical) of the resultant freeze-cast scaffolds. Here, it is proposed that this multitude of techniques and methodologies can be understood from the perspective of two specific groupings:

- Intrinsic control methods that act *within* the freezing process by altering the characteristic repulsive and attractive forces that govern the interactions between the solid loading particles and approaching freezing front during freezing of the slurry.
- Extrinsic control methods that act *upon* the freeze process through the application of additional forces, often external to the freezing process.

Looking to the future, the authors hope that this novel outlook on the freeze-casting process will encourage additional research, specifically into the use of extrinsic methods of control and into interactions between intrinsic and extrinsic methods of control. The vast majority of current freeze-casting research has focused on topics that, given the definitions provided here, would be considered to be intrinsic methods of control, leaving ample space for scientific growth into extrinsic control methods. In addition, while there have

been a number of reports on the understanding of the underlying physics of freeze casting [31,50,51,134,135], there is still plenty of research to be done so as to understand the complex physics that govern the interactions between the entire mass of particles and growing ice that make up the core of freeze casting. Of additional note, while the methods of control described here are presented specifically for their ability to affect freeze casting, the vast majority of them can apply to a wide variety of other fabrication and manufacturing techniques such as particle distribution in polymer-matrix composites and selective solidification of anisotropic metals.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work was financially supported in part by the National Science Foundation under grant CMMI #1660979. The authors wish to thank Profs. Joanna McKittrick and Marc A. Meyers for their guidance on the freeze casting process.

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