Original Article

Microstructural evolution of paramagnetic materials by magnetic freeze casting

Pooya Niksiar\textsuperscript{a}, Michael B. Frank\textsuperscript{b}, Joanna McKittrick\textsuperscript{b, c}, Michael M. Porter\textsuperscript{a, *}

\textsuperscript{a} Department of Mechanical Engineering, Clemson University, Clemson, SC 29634, United States
\textsuperscript{b} Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92039, United States
\textsuperscript{c} Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92039, United States

**Abstract**

External magnetic fields were applied during the process of directional solidification to control the microstructural patterning of ceramic scaffolds formed by freezing colloidal mixtures of magnetic and paramagnetic particles. Under low magnetic fields (<158 mT), uniform and biphasic distributions of magnetite particles (\(\text{Fe}_3\text{O}_4\)) were observed. Uniform distributions of \(\text{Fe}_3\text{O}_4\) formed under low field strengths (<40 mT), while increasing the field strength/gradient (>70 mT) led to the formation of biphasic patterns of iron-rich and iron-poor regions. Under shallow gradients of near-uniform fields, viscous forces dominate, causing the \(\text{Fe}_3\text{O}_4\) particles to remain evenly distributed throughout the slurry. In contrast, larger field gradients exert forces on the \(\text{Fe}_3\text{O}_4\) particles, attracting them toward the magnetic poles. Competition between the viscous and magnetic forces dictates the formation of uniform or biphasic patterning in magnetically aligned freeze cast scaffolds.

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1. Introduction

Freeze casting is a physical process to fabricate lightweight, high-strength materials from particulate matter that mimic the microstructures of natural materials, like nacre or bone [1–3]. This method can be utilized to fabricate polymer [4–6], ceramic/glass [7–10], metal [11–13], and composite [14–17] materials, in which the particulate phase has a relatively low solubility in the freezing vehicle, ensuring expulsion from growing ice crystals during solidification [18–22]. Freeze casting is of interest in many fields, such as chemical analyses [23], cryobiology [24], the food industry [25], and energy storage [26–28]. The exceptional mechanical properties of freeze cast scaffolds are mainly attributed to the complex architecture of their microstructures [18–22]. In this method, ceramic particles are mixed with a freezing vehicle (most often water) that is directionally solidified (see Fig. 1a and b). During freezing, ice columns grow into the form of lamellae and push away colloidal particles, rejecting them from the freezing front [29–31]. Rejected particles are trapped between adjacent ice columns, forming discrete lamellar walls (see Fig. 1b), while secondary dendrites arising from instabilities at the ice front, as well as the engulfment of larger particles (or particle clusters), form mineral bridges connecting adjacent lamellae. After solidification, the frozen materials are lyophilized to remove the ice,
then post-processed (often by heat-treatment or sintering) to strengthen the scaffolds (see Fig. 1c and d).

Ceramic scaffolds formed by freeze casting often exhibit excellent compressive properties in the solidification direction, but lack high strength and stiffness in the transverse direction. To enhance the long-range order and compressive properties in the transverse direction a few approaches have been developed, including architectural patterning [32], bidirectional freezing [33,34], freezing under flow [35,36], and magnetic field alignment [37–41]. In magnetic freeze casting, magnetic or magnetized particles are manipulated by an external magnetic field during solidification [37–41]. The magnetic field causes the magnetic/magnetized particles to reorient or cluster into directionally aligned chains, by similar mechanisms observed in other magnetically-aligned materials [42–46].

In past work, diamagnetic and paramagnetic ceramics mixed with Fe$_3$O$_4$ nanoparticles have shown different behaviors under the influence of external magnetic fields [37,39]. Paramagnetic materials acquire magnetization parallel to the field direction and are attached to higher fields, whereas diamagnetic materials acquire magnetization opposite to the field direction [47]. For mixtures of Fe$_3$O$_4$ nanoparticles with TiO$_2$ (a paramagnetic material with a magnetic susceptibility of +5.9 × 10$^{-6}$ cm$^3$mol$^{-1}$) freeze cast under a field of ∼120 mT, lamellar walls were observed to align parallel to the field, with near-uniform distributions of iron (Fe) throughout the scaffolds [37]. In contrast, comparable mixtures of Fe$_3$O$_4$ with ZrO$_2$ and Al$_2$O$_3$ (diamagnetic materials with susceptibilities of −13.8 × 10$^{-6}$ cm$^3$mol$^{-1}$ and −37.0 × 10$^{-6}$ cm$^3$mol$^{-1}$, respectively), mineral bridges were observed to align parallel to the field (see Fig. 2) [39]; at fields equal to or greater than 120 mT, biphasic patterns formed [37]. These patterns consisted of iron-rich and iron-poor regions, respectively concentrated at the poles and centers of the scaffolds. At the microstructural level, increasing the field strength and Fe$_3$O$_4$ concentration formed longer mineral bridges (in ZrO$_2$-based mixtures) [39]. In either case, alignment of the lamellar walls or mineral bridges resulted in enhanced compressive properties in the transverse direction, parallel to the magnetic field. To better understand the behaviors of paramagnetic materials within mixtures of Fe$_3$O$_4$ particles, we investigated the microstructural evolution of two additional materials, CeO$_2$ and Y$_2$O$_3$ (with magnetic susceptibilities of +26.0 × 10$^{-6}$ cm$^3$mol$^{-1}$ and

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**Fig. 1** — Schematic of the magnetic freeze casting process of ceramic colloids. (a) Ceramic particles are mixed in water; (b) the slurry is placed on a cold surface and ice columns grow directionally, while an external magnetic field aligns magnetic/magnetized particles parallel to the field; (c) the frozen scaffold is placed in a vacuum chamber to sublime the ice, resulting in a porous scaffold; (d) the green body is sintered in a high temperature furnace to strengthen the scaffold.
+44.4 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}, \text{ respectively}, \text{ under similar processing conditions as in previous works} [37–39].

2. Experimental procedure

Ceramic powders of CeO$_2$ and Y$_2$O$_3$ (Sigma Aldrich, St. Louis, MO) used in this study had mean particle sizes of \(~500\) nm (according to the manufacturer). Separate batches of the two powders were suspended in water, similar to previous works [37–39], at fractions of 10 vol.% mixed with 3 wt.% Fe$_3$O$_4$ nanoparticles (\(\sim50\) nm particle size) and 1 wt.% polyvinyl alcohol (PVA) (Alfa Aesar, Ward Hill, MA), polyethylene glycol (PEG) (Alfa Aesar, Ward Hill, MA), and an ammonium polymethacrylate anionic dispersant, Darvan \(^{\text{®}}\) 811 (R. T. Vanderbilt Company, Inc., Norwalk, CT). The slurries were ball milled for 24 h in alumina grinding media, then degassed for 10–20 min and poured into PVC molds attached to a copper cold surface, which was subsequently cooled at a rate of 10 °C min\(^{-1}\). Two 1480 mT permanent neodymium magnets (BY0X08BR-N52, K&J Magnetic, Inc., Pipersville, PA) were oriented transversely across the freezing mold to apply the magnetic fields during solidification (see Fig. 1b). After freezing, the scaffolds were lyophilized at \(-50\) °C and 350 Pa for 72 h using a FreeZone benchtop freeze dryer (Labconco, Kansas City, MO). Finally, the scaffolds were sintered at 1200 °C for CeO$_2$ and 1250 °C for Y$_2$O$_3$ at heating and cooling rates of 2 °C min\(^{-1}\). Finite element models of the magnetic field distributions were developed using FEMM (Finite Element Method Magnetics, David Meeker, Waltham, MA). For more details on the experimental setup, please refer to [37].

3. Material characterization

Optical images were taken with a Wolfe\textsuperscript{®} DigiVu\textsuperscript{™} SMZ 3.0 stereomicroscope equipped with a built-in camera (Carolina Biological Supply Company, Burlington, NC). Scanning electron microscopy (SEM) images were taken at Clemson University’s Advanced Materials Research Laboratory (AMRL) on a Hitachi S-3400N SEM microscope (Hitachi, Schaumburg, IL). Samples were sputter-coated with platinum using a Hummer 6.2 sputtering system (Anatech, Hayward, CA). Energy dispersive X-ray spectroscopy (EDS) was performed to determine the distributions of Fe in the scaffolds. Measurements of the mineral bridges, lamellar walls, and pore widths (Fig. 3) from SEM images of the scaffolds were taken using ImageJ (NIH, Bethesda, MD). The averages and standard deviations were calculated from 50 measurements of each feature.
Fig. 4 – (a) Two locations where SEM images were taken for measurements of the scaffold cross sections; (b) top view, finite element model of the magnetic field applied in the experimental setup; (c) plot of the magnetic field strength along the scaffold height, showing that the magnetic field is stronger at the middle of the scaffolds; (d) plot of the magnetic field strength at the central region of the experimental setup, showing that the magnetic gradient is stronger for the 4.7 cm gap.

4. Results

Fig. 4a shows a schematic of the magnetic field setup. Two locations on the scaffold cross sections were measured: ‘close to the pole’ and at the ‘center’ of the cross section. Fig. 4b shows the field strength between the magnetic poles, approximated by the finite element software, FEMM. Fig. 4c and d shows the variation of magnetic field strength in both the vertical and horizontal directions. Different magnetic field strengths (and gradients) were created by setting the poles 4.7 cm, 7.0 cm, and 10.0 cm apart from each other.

At low magnetic fields (~25 mT), the Fe$_3$O$_4$ nanoparticles were nearly uniformly distributed throughout the CeO$_2$ and Y$_2$O$_3$-based scaffolds (Fig. 5a and c). Increasing the magnetic field strength (~70 mT) resulted in a segregation of Fe$_3$O$_4$ concentrated at the magnetic poles, forming iron-rich and iron-poor regions (Fig. 5b and d). At the microstructural level, the length and thickness of mineral bridges in the CeO$_2$ and Y$_2$O$_3$ scaffolds increased up to a field strength of ~120 mT (see Fig. 6). At fields greater than 120 mT, the mineral bridges tended to decrease in size.

Measurements along the height of the CeO$_2$ scaffolds (Fig. 7a) show a slight decreasing trend for the bridge length versus scaffold height due to the decreasing velocity of the solidification front [48]. In contrast, the bridge thickness shows a slight increasing trend with scaffold height (Fig. 7b), suggesting that as the bridges become shorter, they also become thicker. Notice, Fig. 7a also shows a distinct jump in mineral bridge length at the middle of the scaffold (~18 mm), caused by the stronger field concentrated at the scaffold midsection between the magnetic poles (see Fig. 4c). Additional measurements of the lamellar wall thickness and pore width versus the magnetic field strength (Fig. 8a) show that the external field does not significantly affect these properties. However, these features increase with the scaffold height (Fig. 8b) because of the decreasing velocity of the solidification front [35,49].

5. Discussion

Magnetic freeze casting relies on the use of magnetic fields to manipulate matter during the solidification of colloidal suspensions. Although water is a diamagnetic material, its magnetic susceptibility is relatively small, and weak magnetic fields, such as those investigated here, have a minimal effect [50]. Nevertheless, Tang et al. [51] recently showed that magnetic fields weaken the hydrogen bonds between clusters of water molecules, leading to the growth of smaller ice crystals, and hence decreased pore sizes (in diamagnetic slurries). To a similar effect, we observed a small decreasing trend in pore size with increasing field strength (see Fig. 8a). However, in this study, the magnetic response of the magnetite and paramagnetic particles tend to dominate over the molecular restructuring of water. When magnetic dipoles (such as those in the Fe$_3$O$_4$ nanoparticles of this study) are placed in a magnetic field, a torque and force are exerted on them. The torque rotates the dipoles and aligns them in the direction of
Fig. 5 – Magnetic freeze cast scaffolds of CeO₂ and Y₂O₃ containing 3 wt.% Fe₃O₄. Y₂O₃ freeze cast under (a) 25 mT and (b) 42 mT; CeO₂ under (c) 25 mT and (d) 71 mT. Orange arrows show the direction of the magnetic field; in (b) and (d) the white regions are iron-poor and the orange/purple regions are iron-rich; and the insets (e and f) show elemental mappings at the Fe-poor/rich boundary for Y₂O₃ and CeO₂, respectively, where black and red/orange colors represent Fe-poor and Fe-rich regions.

Fig. 6 – Mineral bridge (a) length and (b) thicknesses of CeO₂ and Y₂O₃ scaffolds as functions of magnetic field strength for the two different locations on the cross section: 'close to pole' and 'center' (see Fig. 4a). CeO₂ measurements are done at 10 mm height from the bottom of the scaffold (of 25 mm length scaffolds) and Y₂O₃ measurements are done at 18 mm height for both graphs. Error bars show confidence intervals for 95% probability.

Fig. 7 – Mineral bridge (a) lengths and (b) thicknesses of CeO₂ scaffolds are measured as a function of height for the 25 mT and 71 mT fields. Measurements are from the ‘center’ location. Error bars show confidence intervals for 95% probability.
the magnetic field, often forming chain-like particle clusters. The magnitude of the torque is [47]:

$$N_B = m \times B$$  \hspace{1cm} (1)

where $m$ is a magnetic dipole moment and $B$ is the magnetic field strength. The magnetic force in the horizontal direction acting on a particle suspended in a liquid is [52,53]:

$$F_B = V_P \left( \frac{1}{\mu_0} \right) (\chi_P - \chi_M)B \left( \frac{dB}{dx} \right)$$  \hspace{1cm} (2)

where $V_P$ is the volume of the particle, $\mu_0$ is the vacuum permeability $(4\pi \times 10^{-7} \text{ H m}^{-1})$, $B$ is the magnetic field strength, and $\chi$ is the magnetic susceptibility where $M$ denotes the matrix (liquid), and $P$ denotes a particle. Here, because gravity is oriented perpendicular to the magnetic force, it is neglected. When aligning magnetic (or surface-magnetized) particles parallel to a magnetic field, the magnetic torque competes with the random thermal motions of the particles and fluid viscosity [40,41]. Under lower magnetic fields, the torque cannot overcome thermal agitation or viscous forces, resulting in little to no microstructural alignment. At higher field strengths, however, the torque can overcome these forces, resulting in greater particle clustering, chaining, and alignment (under near-uniform fields). The increased apparent size of particle chains/clusters leads to a greater frequency of particle entrapment (see Fig. 9). This phenomenon was recently observed in the formation of aligned mineral bridges from mixtures of ZrO$_2$ and Fe$_3$O$_4$ particles freeze cast under fields of varying strength (0–90 mT) [39]. In contrast, surface-magnetized Al$_2$O$_3$ particles of varying size freeze cast under a range of fields (0–150 mT), showed significant lamellar wall alignment at a critical particle size (350 nm) and field strength (75 mT) [41]. In this case, the magnetized particle chains/clusters act as templates for ice nucleation, guiding the alignment of directional ice columns. Although not yet confirmed, a similar nucleation-alignment mechanism is likely responsible for the lamellar wall alignment observed in experiments with mixtures of TiO$_2$ and Fe$_3$O$_4$ particles [37].

As seen in Eqs. (1) and (2), the magnetic torque is dependent on the magnetic field strength, while the magnetic force is dependent on both the magnetic field strength and gradient. For the 10.0 cm gap, the magnetic field gradient (VB) was approximately 0.17 T m$^{-1}$, while for the 4.7 cm gap it was around 2.0 T m$^{-1}$, an order of magnitude greater. This larger gradient produces a stronger force on the magnetic dipoles, causing a migration of Fe$_3$O$_4$ particles toward the poles, which requires them to overcome the opposing viscous forces. For a spherical particle moving through a fluid, the viscous force is given by the modified Stokes’ equation [49]:

$$F_f = \frac{6\pi \mu_0 v_r}{r}$$  \hspace{1cm} (3)
where $\mu$ is the viscosity of the fluid, $r$ is the diameter of a particle, $v$ is the velocity of a particle relative to the fluid, and $f$ is a dimensionless friction factor [49]. In the case that $F_v$ is small compared to $F_f$, the Fe$_3$O$_4$ particles will not move toward the magnetic poles (alternatively, the relaxation time necessary for the Fe$_3$O$_4$ particles to reach the poles is large compared to the time it takes them to transfer through the well-mixed slurry before freezing) such that a uniform iron distribution is observed (see Fig. 5a and c). In the case that $F_v$ is large compared to $F_f$, the Fe$_3$O$_4$ particles migrate toward the magnetic poles, forming the iron-rich and iron-poor regions (see Fig. 5b and d). Thus, increasing the magnetic field strength increases the magnetic torque, resulting in an increased length of mineral bridges. Beyond a specific field strength (>120 mT for CeO$_2$), the mineral bridge length decreases as the magnetic force becomes dominant and pulls the Fe$_3$O$_4$ particles toward the poles (see Fig. 6a). In contrast, lower magnetic fields (<40 mT) produce shallower gradients, which lead to negligible magnetic forces on the Fe$_3$O$_4$ particles, leading to the near-uniform Fe distributions.

6. Conclusions

In this study, we showed that either uniform or biphasic patterns can be developed in mixtures of paramagnetic (CeO$_2$ or Y$_2$O$_3$) and magnetic (Fe$_3$O$_4$) particles by magnetic freeze patterning. We suggest that the formation of uniform versus biphasic patterns is dependent on the magnetic field strength and gradient, plus the magnetic susceptibility and density of the particles. Because CeO$_2$ and Y$_2$O$_3$ have larger magnetic susceptibilities than TiO$_2$ [54], they induce a larger magnetization within the slurry which exerts greater forces on the Fe$_3$O$_4$ particles. Particle density variations (TiO$_2$ = 3.78 g cm$^{-3}$; CeO$_2$ = 7.22 g cm$^{-3}$; Y$_2$O$_3$ = 5.01 g cm$^{-3}$) may also affect sedimentation prior to freeze casting, leading to non-uniform distributions of Fe$_3$O$_4$ in the slurry. Measurements of the lamellar walls and pore widths show that external magnetic fields do not substantially affect the freezing liquid properties. Instead, external magnetic fields primarily affect the formation of mineral bridges (as shown in Fig. 2b) where Fe$_3$O$_4$ particles tend to accumulate into clustered chains within the bridges. At higher field strengths, magnetic field gradients produce biphasic patterns, similar to those seen in ZrO$_2$, Al$_2$O$_3$ and hydroxyapatite (diamagnetic) scaffolds [37]. At the microstructural level, increasing the magnetic field up to ~120 mT, increased the mineral bridge length, but >120 mT decreased the bridge length because of the migration of Fe$_3$O$_4$ particles toward the magnetic poles. Thus, it is suggested that these variations in microstructural patterning are the result of competition between the magnetic force, torque, and susceptibility, particle size and density, thermal energy, and viscous forces on the colloidal particles.

Conflicts of interest

The authors declare no conflicts of interest.

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