Freeze-Cast Alumina Pore Networks: Effects of Freezing Conditions and Dispersion Medium

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Abstract

Alumina ceramics were freeze-cast from water- and camphene-based slurries under varying freezing conditions and examined using X-ray computed tomography (XCT). Pore network characteristics, i.e., porosity, pore size, geometric surface area, and tortuosity, were measured from XCT reconstructions and the data were used to develop a model to predict feature size from processing conditions. Classic solidification theory was used to examine relationships between pore size, temperature gradients, and freezing front velocity. Freezing front velocity was subsequently predicted from casting conditions via the two-phase Stefan problem. Resulting models for water-based samples agreed with solidification-based theories predicting lamellar spacing of binary eutectic alloys, and models for camphene-based samples concurred with those for dendritic growth. Relationships between freezing conditions and geometric surface area were also modeled by considering the inverse relationship between pore size and surface area. Tortuosity was determined to be dependent on the type of dispersion medium alone, independent of temperature parameters.

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1. Introduction

Porous ceramics are attractive materials for use in filters, thermal insulation, and energy devices due to their chemical inertness, low thermal conductivity, and solid-state ionic conductivity.[1, 2] Freeze casting, shown schematically in Figure 1, has been used as a method for making porous ceramics with directional pores by loading a liquid dispersion medium with ceramic particles and freezing the slurry on a cold surface. During solidification the particles are ejected from the freezing front and compacted between adjacent crystals.[3] The template crystals are removed via sublimation before sintering the remaining ceramic green body to make a robust porous monolith.[3] Pores within the structure are negative copies of the solidified dispersion medium. The variety of controllable processing variables promises the ability to make tailored porous ceramic structures.

Characterization of pore networks of directional freeze-cast ceramics to date has been largely focused on porosity and pore size, and their effect on mechanical properties.[4-8] Porosity increases with decreasing solids loading in a linear manner. Pore size decreases with increased freezing front velocity, i.e., the speed at which the solid-liquid interface advances, which increases with decreasing freezing surface temperature.[3, 5, 9-11]

In addition to porosity and pore size, other pore network characteristics such as morphology, tortuosity, and pore orientation also significantly influence application-specific properties like permeability and geometric surface area.[12, 13] Pore morphology is dependent primarily on the dispersion medium; for example, samples cast from water-based slurries have lamellar pores,

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4 camphene-based slurries result in dendritic pores, and tert-butyl alcohol-based samples have
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6 prismatic pores.[3, 14] Dispersion media themselves can also be altered by inclusion of additives
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8 designed to alter the freezing temperature, pH, or viscosity of the liquid.[3] Control over surface
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10 area and tortuosity has not been established or well-studied.
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14 The ability to use freeze-cast products commercially requires easy fabrication and increase in
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16 production scale. If small-scale freeze casting is considered as a volume element of a large scale
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18 production process, the ability to predict pore network characteristics without iterative testing in
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20 a specially designed casting setup becomes possible. As such, the overarching purpose of this
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22 study is to describe the development of and results for freeze casting models that will allow
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24 researchers to determine processing conditions required to yield a set of pore network
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26 characteristics *a priori*. Since pore size in freeze-cast samples is reportedly influenced by
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28 freezing front velocity, a pore size model must include a method of predicting freezing front
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30 velocity from freezing conditions, a requirement that will be satisfied using the two-phase Stefan
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32 problem. Traditional solidification theory will subsequently be used to describe relationships
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34 between feature size and freezing conditions. The two parts are then combined and applied to
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36 freeze casting. Pore size data measured from freeze-cast samples will be presented and used in
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38 development of the model. Pore size models are then extended to geometric surface area and
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40 tortuosity using geometric considerations, and validated using the data collected.
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2. Experimental Methods and Model Development

2.1 Experimental Methods

2.1.1 Materials

Slurries were made using calcined 0.35 μm α -alumina with 300 ppm MgO (Baikowski Malakoff, Inc., Malakoff, TX, USA) with 23 vol.% solids loading for water-based and 22 vol.% for camphene-based samples.[15] Dispersion media of deionized water or (–)-camphene (technical grade, >78%(–)-camphene, remainder the isomer α -fenchene and other unidentified tricyclene isomers of camphene, Alfa Aesar, Ward Hill, MA, USA) were the balance of the slurry volume. Water-based slurries also included 3 wt.% (of the solids) Darvan 811 (sodium polyacrylate, Vanderbilt Minerals, LLC, Norwalk, CT, USA) anti-flocculation dispersant. Dispersant added to camphene-based slurries was 3 wt.% (of the solids) Hypermer KD-4 (polymeric surfactant, Croda Inc., Edison, NJ, USA). Addition of the dispersants did not significantly alter slurry solids loading. Slurries were ball-milled for 24 hours at room temperature and at 60°C for water- and camphene-based slurries, respectively, before casting. After samples were frozen water-based castings were placed in a freeze dryer for 24 to 48 hours to remove the solidified dispersion medium. Camphene-based castings were left in a fume hood at ambient conditions for the same period. [16-18] No sample deformation was observed during the drying stage for either type of sample. Finally, samples were sintered at 1600°C for 5 hours with ramp rates of 5°C/min from room temperature.

2.1.2 Casting Setup

The casting setup was constructed using ABS piping components, PEX tubing, and expanding spray foam insulation. The PEX tubing sample holders had a 2.2 cm inner diameter with 0.85 cm walls. Between approximately 8 and 12 mL of slurry per sample was frozen on a

thermoelectric cooler (TEC) module (TE Technology, Inc., Traverse City, MI, USA) placed on top of a water-chilled cold plate. Temperature of the TEC surface was adjusted by varying voltage supplied to the TEC, and was monitored with a K-type thermocouple placed on top of the cold TEC surface. A schematic of the casting setup is shown in Figure 2. The slurry, sample holder, and insulating setup were cooled or heated to the desired starting temperature (T_{Hot}) before casting; likewise, the TEC freezing surface was pre-chilled to the desired freezing temperature (T_{Cold}). Table 1 is a summary of the initial slurry temperatures and freezing temperatures used. The melting temperatures, T_m , of water and camphene were assumed constant, and equal to 0 and 35°C, respectively.[19]

2.1.3 Sample Characterization

Pore network characteristics reported in this study (pore size and lamellar spacing, geometric surface area, and tortuosity) were measured from segmented images obtained from X-ray computed tomography (XCT) reconstructions. XCT was performed at beamline 2-BM at the Advanced Photon Source at Argonne National Laboratory.[20] Cylindrical samples ~3 mm in diameter for X-ray tomography scanning were cut from the top third of epoxy-mounted samples, 15 to 17 mm from the freezing surface. Samples were placed 5 mm from the detector and scanned with 27.39 keV X-rays, capturing radiographs with a 2048 x 2048 pixel Coolsnap K4 CCD detector using a 5x lens. A 3-layer paper diffuser was used to smooth the X-ray beam background. Voxel size was $(1.45 \mu\text{m})^3$ resulting in a resolution of about 3 μm . Radiographs were acquired using a 250 ms exposure every 0.12 degree over a 180 degree rotation, and each sample took approximately 30 minutes to scan. The two-dimensional cross-section slice images 2048 x 2048 pixels (3 mm x 3 mm) in size were reconstructed using an algorithm provided at the 2-BM beamline.[20-22] Binary segmentation was performed on the reconstructed XCT images

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4 using MATLAB[®] (The MathWorks, Inc., Natick, MA USA) after equalizing the grayscale
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6 images using ImageJ software (National Institutes of Health).[23] Median image filters built into
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8 MATLAB[®] were applied to remove noise from the segmented images. Three-dimensional
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10 reconstruction volumes analyzed were as large as 978.75 x 978.75 x 1450 μm^3 . All pore network
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12 measurements were done in MATLAB[®].
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16 Due to the dissimilar pore morphologies of water-based and camphene-based samples,
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18 measurement techniques for pore size were customized for each. Pore size measurements for
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20 both sample types were taken from a series of 50 cross-sections perpendicular to the freezing
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22 direction. Fifty equally-spaced slices per sample were analyzed; vertical distance between the
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24 analyzed cross-sections depended on sample height and varied between 10 and 36 μm . Pore size
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26 for water-based samples was considered to be the width between adjacent ceramic walls, w , and
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28 was measured by a Euclidean distance mapping and skeletonization technique imposed on each
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30 image. Lamellar spacing of water-based samples, λ , was measured by calculating width of the
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32 ceramic walls using the same Euclidean distance mapping and skeletonization technique and
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34 adding the median pore width to the median ceramic wall width. In contrast, the 2D Münch &
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36 Holzer method was used to measure the irregularly shaped pores in camphene-based samples,
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38 describing them as the diameter of a comparative circular pore, d . [24] Both water- and
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40 camphene-based pore size measurement techniques provide a pore size distribution measurement
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42 for each sample and pore size reported is the median value of the distribution.
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51 Geometric surface area for both water-based and camphene-based samples was measured in
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53 3D from XCT images using a marching cubes algorithm in conjunction with a mesh surface
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55 measurement algorithm, implemented in MATLAB[®]. [25, 26] Surface area measured was
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57 normalized by the total pore volume in each data set.
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Tortuosity was also measured for both sets of samples and is defined as the ratio of the tortuous geodesic length, L , to the direct Euclidean length, R , between points A and B, demonstrated schematically in Figure 3. Tortuosity for water-based lamellar-type channels was measured from 2D longitudinal cross-sections parallel to the freezing direction due to the simplicity of the lamellar pore morphology. Twenty cross-sections were analyzed over a total sample width of 1.45 mm. Calculations were performed on paths between nodes at the top and bottom of the images and the tortuosity along channels was determined. Tortuosity measurements for camphene-based samples were performed in 3D using Amira[®] 5 software (Visualization Sciences Group, an FEI Company, Burlington, MA USA) and MATLAB[®]. Pore centerlines along the length of the sample, ultimately defining the pore structure, were identified using Amira[®] 3D skeletonization algorithms. The set of centerline nodes describing the sample pore structure was then imported into MATLAB[®], where tortuosity was calculated using the Dijkstra algorithm, applied between nodes on the top and bottom slices only, again to account for pore directionality.[27, 28] The overall minimum tortuosity measurement is reported for both water- and camphene-based samples.

2.2 Model Development

2.2.1 Solidification Theory and Application to Freeze Casting

Solidification of pure materials and binary alloys has been studied since the 1940s. [29-31] Theories for lamellar, cellular, and dendritic structures indicated that growth velocity, V , temperature gradient, G , and solute gradients (if applicable, not included here) were the primary factors dictating dendrite or cell and lamellar spacing:

$$\lambda_L \propto V^{-1/2} \quad (1)$$

$$\lambda_c \propto V^{-1/2} \quad (2)$$

$$\lambda_1 \propto V^{-1/4} G^{-1/2} \quad (3)$$

where λ_L is lamellar spacing, λ_c is cell width, and λ_1 is primary dendrite spacing.[30, 32, 33]

Strictly theoretical equations describing secondary dendrite arm spacing, λ_2 , with solidification conditions have not been developed. However, Kirkaldy *et. al.* determined experimentally that equations describing λ_2 took the same form as the Mullins and Sekerka marginal stability wavelength, and heuristically established the relationship:

$$\lambda_2 \propto V^{-2/3} \quad (4)$$

where temperature gradient is considered constant.[34] It is expected that temperature gradient would be included in Equation 4 if varied experimentally. Equations 1 – 4 will be used to describe pore size of freeze-cast samples based on pore morphology.

Several authors have referenced similarities between freeze casting and freezing of pure, dilute, and binary systems due to solidification morphology.[5, 10, 11, 35, 36] The similarities between them can be viewed by assuming that the ceramic particles act as a “solute” in the dispersion medium “solvent”, and must be ejected from “solution”. The “solute” particles are ejected until none remain in the pure dispersion medium “solvent”, and become concentrated in “solution” between adjacent crystals until all liquid is frozen. In this way, freeze casting can be likened to both lamellar and dendritic material solidification. The structure of the solidified dispersion media in freeze-cast samples spurs the association of water-based samples to solidification of substances resulting in lamellar structures, i.e., eutectic alloys, and camphene-based samples to dendritic solidification of pure materials or alloys. Lamellar spacing (λ) and pore width (w) for water-based samples may be likened to eutectic lamellar spacing (λ_L) or cell width (λ_c), respectively. Pore diameter in camphene-based samples (d) may be likened to

secondary arm dendrite size (λ_2) as the pores measured are negative templates of the secondary arms of the solid camphene, a conclusion supported by previous studies.[35, 37]

2.2.2 The Two-Phase Stefan Problem and Design Adjustments

The two-phase Stefan problem (TPSP) describes directional solidification of a semi-infinite uniformly heated ($T_{Hot} > T_m$) pure melt from a cold boundary ($T_{Cold} < T_m$) over time, with conservation of energy across the interface (the Stefan condition). [38] Supplemental materials in section S1 further describe the setup of the TPSP. The Neumann solution to the TPSP provides an equation for the velocity of the freezing front during solidification, given by:

$$V(t) = \Lambda \sqrt{\alpha_s/t} \quad (5)$$

where Λ is solved using:

$$\Lambda \sqrt{\pi} = \frac{St_s}{\exp(\Lambda^2) \operatorname{erf}(\Lambda)} - \frac{St_l}{\mu \nu \exp(\mu^2 \nu^2 \Lambda^2) \operatorname{erfc}(\mu \nu \Lambda)} \quad (6)$$

with $St_s = c_p^s(T_m - T_{Cold})/L$, $St_l = c_p^l(T_{Hot} - T_m)/L$, $\mu = \rho_s/\rho_l$, $\nu = \sqrt{\alpha_s/\alpha_l}$, and $\alpha = k/\rho c$. Density, ρ , thermal conductivity, k , and heat capacity, c_p , are those of the solidifying material before (subscript l) and after (subscript s) freezing. L is the latent heat of fusion of the material. Density, thermal conductivity, and heat capacity values are combined to obtain the thermal diffusivity of the material, $\alpha_{l/s}$. The ratio μ is included in Equation 6 to account for the difference in density between the solid and the liquid. Temperature-dependent thermal and physical property values for each sample type are used here in the TPSP solutions at T_{Hot} and T_{Cold} .

The TPSP assumes that the freezing liquid is a pure material, indicating that some additional adjustments and assumptions may be required to apply it to freeze casting, summarized here.

Densities of solid and liquid slurries were estimated using the volume fraction rule of mixtures

between alumina ($\rho_{Al_2O_3} = 3.98 \text{ g/cm}^3$) and the dispersion medium.[15] Thermal conductivity of liquid suspensions were approximated as the thermal conductivity of a random suspension of spheres, developed by Jeffrey.[39, 40] The treatment assumes a stationary and homogeneous suspension of randomly distributed identical spherical particles in an infinite dispersion medium where the volume fraction of particles is small enough that interactions between particles are negligible[#]. Thermal conductivity of alumina was between 28 and 71 W/m-K in the range of the T_{Hot} and T_{Cold} temperatures used.[41] Alternatively, thermal conductivity of the solid after freezing was approximated as thermal conductivity of a composite with lamellae or rods oriented along the direction of the heat flux, and was calculated using the volume fraction rule of mixtures.[42, 43]

Heat capacities of liquid slurries were estimated using the mass fraction rule of mixtures, as this method has been used to calculate the specific heat of nanoparticle suspensions.[44] Heat capacities of the frozen slurries, again modeled as composites, were also estimated using the mass fraction rule of mixtures.[43] Values for the heat capacity of alumina were between 0.593 and 0.807 J/g-K for the temperature parameters used.[41]

Latent heat of fusion values for both slurry types were estimated by assuming that only the dispersion medium contributes to the energy released upon solidification, a reasonable assumption as the alumina particles do not undergo any phase changes over the temperature ranges explored here. The latent heats of fusion for the slurries are estimated using:

$$L_{slurry} = (1 - \phi) \rho_l L / \rho_{slurry(l)} \quad (7)$$

[#] Though Jeffrey's definition is considered applicable only for solids loading of 10 vol.% or less, calculations for $k_{slurry(l)}$ using a more detailed model developed by Chiew and Glandt for solids loading greater than 10 vol.% changed $k_{slurry(l)}$ values by only 1%. Calculated A_{slurry} changed by less than 0.1%, justifying the use of Jeffrey's method here.

where ρ_l and $\rho_{slurry(l)}$ are the densities of the liquid dispersion medium and slurry, respectively, and L is the latent heat of fusion for the pure dispersion medium.

Thermal and physical properties for pure dispersion media were obtained through the literature. Temperature-dependent equations were employed when available, as regression models using temperature-dependent thermal and physical properties had higher adjusted R-squared values compared to those calculated using constant temperature values.

Values for density, thermal conductivity, heat capacity, and latent heat are listed in Table 2 for pure dispersion media and slurries at the maximum T_{Hot} and minimum T_{Cold} for each type of sample. The camphene used here is >78% (-)-camphene. If data were not available or measured for the camphene of the purity used here, thermophysical values required for the TPSP were adopted from those for pure (-)-camphene or pure ($\pm$)-camphene.[45-48]

The physical and thermal property values from Table 2 for both pure dispersion media and slurries were substituted into the TPSP Neumann solutions to get $V(t)$ equations for the dispersion media and the slurry. For both sample types, using calculated thermal and physical properties of the slurry resulted in higher A values compared to that of the pure dispersion medium, increasing by 25 to 31% for water-based samples and by 23 to 55% for camphene-based samples. This increase in A values, which indicates higher freezing front velocities, suggests that the ceramic particles may significantly contribute to the physics of freeze casting.

2.2.3 Combining Solidification Theory with the TPSP

Pore size in freeze-cast ceramics is known to increase as freezing progresses due to a gradual decrease in freezing front velocity. However, by measuring pore network characteristics from sample sections towards the end of the freezing process, steady state velocity can be assumed, which would allow the use of A , from the TPSP, in place of V , from solidification theory. To

support this assumption, velocity was calculated using the TPSP equation at and after 45 minutes for water and 30 minutes for camphene, which is within the range of freezing times observed for all samples. Changes in calculated velocity over this range of time were minimal, decreasing by 5% or less for water every 5 minutes after 45 minutes of freezing and by 7% or less for camphene every 5 minutes after 30 minutes of freezing. *In-situ* temperature measurements during solidification of a similar slurry in a parallel system also indicated that steady state freezing had been reached. Temperature gradient in solidification theory is replaced by the temperature gradient applied to each sample, G_{app} , and is defined as the vertical temperature gradient present when the slurry is cast:

$$G_{app} = (T_{Hot} - T_{Cold})/l \quad (8)$$

where l is the height of each sample as poured into the sample holder before casting. These substitutions into the solidification model equations in Equations 1 through 4 allow the comparison of well-established solidification models to freeze casting to determine how pore network characteristics are influenced by A and G_{app} . Also note that regression equations reported do not include constants, as they are the statistically identically between each set of equation comparisons (dispersion medium versus slurry).

3. Results and Discussion

3.1 Pore Network Measurements

Representative images of the samples cast in this study are shown in Figure 4. Figures 4a, c, and e are from water-based samples shown parallel and perpendicular to the freezing direction with a 3D reconstruction, respectively. Figures 4b, d, and f are the same respective orientations for camphene-based samples.

Sintered samples were 2.0 to 2.4 cm tall. Archimedes' density measurements on sintered water- and camphene-based samples gave $63.9 \pm 1.4\%$ and $63.6 \pm 1.2\%$ porosity, respectively.[49] XCT calculations showed $62.0 \pm 3.2\%$ porosity in water-based samples and $60.9 \pm 1.4\%$ porosity in camphene-based samples. The XCT porosity calculations are in good agreement to those measured using the Archimedes' density method. The slight lower calculated porosity in camphene-based samples may come from the exclusion of pores smaller than the spatial resolution available in XCT measurements.

Table 1 includes a summary of pore size, geometric surface area, and tortuosity measurements from XCT image analysis for each sample.

3.2 Pore Size Models

Pore size equations for water-based samples determined by regression analysis are similar to the relationships between freezing conditions and feature size established from solidification theory and experimental data for aqueous solutions and lamellar eutectic binary alloys.[33, 50] Specifically, pore size was dependent only on λ and there was no statistically significant dependence of pore size or lamellar spacing on G_{app} . Regression models for camphene-based samples are similar to models established theoretically and other regression models determined experimentally for dendritic substances, and were dependent on both λ and G_{app} . [51, 52] Table 3 is a summary of the regression models for pore size of both water- and camphene-based samples using λ_{dm} or λ_{slurry} that were statistically significant with over 95% confidence and had an adjusted R-squared value over 80%, where the subscripts *dm* and *slurry* indicate whether λ was calculated using thermophysical properties of the dispersion medium or the slurry, respectively. Table 3 also includes the P-values and adjusted R-squared values for the models. Figure 5 shows graphical representations of the equations in Table 3.

For water-based samples, a two-sample Z-test indicated that the exponents for A_{dm} and A_{slurry} were not statistically different using $\alpha = 0.05$. Considering the relatively large confidence intervals for the exponent values, this is not unexpected. However, A_{dm} and A_{slurry} exponents for camphene-based samples had smaller confidence intervals, and are statistically different, though the calculated Z value is close to the critical Z value. Exponents (m) for G_{app} are considered identical. All models using A_{dm} had slightly higher adjusted R-squared values than models calculated using A_{slurry} , by as much as 1.3%. P-values remained consistent between the two A options. Adjusted R-squared values for both sample types indicate that A_{dm} a better fit when describing the correlations between pore size and A in the current casting setup. Likewise, standard errors of A calculated during regression analysis (not show) for dispersion media models are smaller than those for slurry models. The increase in A between using dispersion media properties versus those calculated for the slurries, better regression fits, and smaller standard errors using A_{dm} indicate that actual freezing rates are closer to those predicted using properties of the dispersion media alone. While including slurry properties in the TPSP calculations attempts to reduce the assumptions made to compare freeze casting of ceramics to traditional solidification, it introduces numerous other assumptions about the slurry itself. It is possible that, if spatially and temporally exact properties of the slurry were known, the regression equations would differ. However, results in this study indicate that including slurry properties in calculations is unnecessary, and using properties of the dispersion media is sufficient.

Trends in experimental data describing feature sizes resulting from processing conditions from numerous metal solidification studies agree well with theory, with exponents ranging between -0.5 and -0.7 for lamellar structures and between -0.3 and -0.5 (both exponents) for

dendritic structures.[53] Additionally, application of theoretical models to non-metallic materials like cyclohexanol and succinonitrile resulted in regression equations with similar exponents to those calculated for metals, indicating that theory-derived solidification models could be applied to a wide array of material systems.[51, 54]

In addition to agreeing with numerous models given in the literature for traditional solidification studies, the pore size models calculated here are similar to previous studies of freeze-cast ceramics investigating the correlations between pore size of water- or camphene-based samples and freezing temperature or freezing front velocity. Deville et al. measured lamellar spacing of water-based freeze-cast samples in a steady state region and compared values to estimated freezing front velocities. The power law relationship between lamellar spacing and freezing front velocity they calculated, with exponents ranging from -0.67 to -1 and varying with ceramic particle size, was similar to the model calculated here.[11] Another study by Bareggi et al. measured freezing front velocity from X-ray radiographs for specific temperature settings and compared measured velocity to theoretical velocity calculated using the two-phase Stefan problem, but did not measure lamellar spacing of the resulting structures.[9] Shanti et al. assumed that freezing front velocity was inversely proportional to the height of the frozen zone in freeze-cast samples, and matched their pore size measurements for camphene-based samples to a solidification power law for metals with an exponent of -1/3.[35, 55] The regression coefficients calculated here for camphene-based samples are similar to those determined by Çadırli et al., who measured the dendrite characteristics of pure camphene as a function of freezing conditions, with n and m equal to 0.31.[52] Similarly, Rohatgi and Clyde calculated exponents for binary aqueous solutions, equal to -0.5.[50] The studies by Rohatgi and Clyde, and Çadırli et al. further encourage comparisons between freeze casting and traditional solidification.

3.3 Geometric Surface Area Models

It is known that geometric surface area should increase with decreasing pore size. To verify this, regression analysis was performed between measured geometric surface area (GSA) and pore size or lamellar spacing, resulting in the following models:

$$GSA \propto \lambda^{-1.52 \pm 0.14} \text{ (water-based)} \quad (9)$$

$$GSA \propto w^{-1.28 \pm 0.09} \text{ (water-based)} \quad (10)$$

$$GSA \propto d^{-0.84 \pm 0.19} \text{ (camphene-based)} \quad (11)$$

Equations 9 and 10 had adjusted R-squared values greater than 98%. Equation 11 had an adjusted R-squared value of 96%. All models had P-values less than 0.001. These results indicate that statistically significant regression models connecting GSA to λ or λ and G_{app} may exist. Additionally, since pore size and surface area are inversely related, the exponents for power law models between GSA and λ or λ and G_{app} are expected to be positive. Regression analysis confirmed this, and the resulting models are listed in Table 4. Similar to models for pore size, exponents for the water-based GSA regression models using λ_{dm} are not statistically different from those using λ_{slurry} , whereas those for λ values in camphene-based sample models are. Temperature gradient exponents are not statistically different. Figure 6 shows graphically the regression models in Table 4 for both sample types.

Figure 6 shows that camphene-based samples had higher geometric surface area than water-based samples despite similar pore sizes (width and diameter). This is an expected result due to the dendritic nature of the pores in camphene-based samples. Thus in addition to pore size, pore morphology is important when considering freeze-cast ceramics for use as catalyst supports and in other applications which require high surface area.

3.4 Tortuosity Models

Camphene-based samples were overall more tortuous than water-based samples ($\tau = 1.3$ to 1.5 vs. 1.1, respectively). Visually examining the XCT images, it is clear that pore morphology is similar on all size scales for the respective sample types, appearing to be unrelated to freezing conditions. Regression analysis confirmed that neither A nor G_{app} influenced tortuosity for water-based samples, a logical conclusion given the naturally well-aligned pore structure. For camphene samples, both linear (with a negative slope) and inverse power law regression models of tortuosity and G_{app} were statistically significant, with P-values < 0.05 but adjusted R-squared values of between 60 and 65% (recall that the earlier regression models have adjusted R-squared values above 80%). Both models indicate that tortuosity decreases as G_{app} increases. Increased G_{app} is expected to enhance pore alignment due to the larger thermal driving forces present, implying that tortuosity is inversely related to pore alignment, a conclusion supported by the lower tortuosity and increased pore alignment of lamellar water-based samples compared to camphene-based samples. Although tortuosity may be tailored primarily by choice of dispersion medium, and hence pore morphology, the above tortuosity models indicate that tortuosity may be adjusted by altering the applied temperature gradient.

4. Conclusions

This study demonstrates how pore size and geometric surface area of freeze-cast alumina ceramics in a steady-state regime can be predicted from models developed by combining traditional solidification theory with the two-phase Stefan problem. Water- and camphene-based slurries with 23 and 22 vol.% solids loading alumina, respectively, were cast under varying temperature conditions and analyzed for porosity, pore size, geometric surface area, and tortuosity from X-ray computed tomography 2D images and 3D reconstructions.

The Neumann solution of the two-phase Stefan problem was used to obtain a prediction of the magnitude of steady-state freezing front velocity, $\dot{A}$. Combining the solution with theoretically-derived relationships between feature size and freezing conditions for lamellar and dendritic materials, regression models were developed correlating pore size with $\dot{A}$ or $\dot{A}$ and applied temperature gradient, G_{app} . Models for water-based slurries took the same form as those developed using solidification theory for lamellar microstructures. Likewise, models for camphene-based slurries had the same form as theories for dendritic microstructures. Furthermore, the exponents in the regression models matched those in the theoretically-derived solidification models and were similar to those reported in numerous solidification studies of metallic and non-metallic materials, alloys, and solutions.

The correlation between pore size and surface area was used to predict the existence of relationships between geometric surface area and $\dot{A}$ or $\dot{A}$ and G_{app} . Surface area models took the form of positive power laws, as expected from the inverse relationship between pore size and freezing conditions described above. Camphene-based samples had overall higher geometric surface area measurements than water-based samples due to the dendritic versus lamellar pore morphology.

It was found that using the physical and thermal properties of the dispersion medium alone, including density, thermal conductivity, heat capacity, and heat of fusion, provided as much or more accuracy in predicting pore size and geometric surface area from freezing conditions compared to using calculated estimates of the physical and thermal properties of the slurries.

Finally, tortuosity was determined to be independent of freezing conditions for water-based samples. Tortuosity in camphene-based samples was higher than that in water-based samples, a conclusion supported by the differences in pore morphologies. Findings indicated that

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S1. Supplemental Material: Derivation and Solutions of the Two-Phase Stefan Problem

One mathematical model of freezing a heated melt from a cold boundary is the two-phase Stefan problem (TPSP). The TPSP setup is shown schematically in Figure S1. Using classic heat equations in the solid and liquid, assuming constant interface temperature equal to the melting temperature, and applying the Stefan condition, boundary conditions, and initial conditions, the solution, known as the Neumann solution, to describe spatially- and temporally-dependent temperature fields in the solid and liquid phases, $T_{s/l}(z, t)$, as well as the solid/liquid interface position over time, $X(t)$, can be obtained, given in Equations S1 – S3.[38, 57]

$$T_s(z, t) = T_{Cold} - (T_{Cold} - T_m) \operatorname{erf}\left(\frac{z}{2\sqrt{\alpha_s t}}\right) / \operatorname{erf}(\Lambda), \quad z < X(t) \quad (\text{S1})$$

$$T_l(z, t) = T_{Hot} + (T_m - T_{Hot}) \operatorname{erfc}\left(\frac{z}{2\sqrt{\alpha_l t}}\right) / \operatorname{erfc}(\nu\Lambda), \quad z > X(t) \quad (\text{S2})$$

$$X(t) = 2\Lambda\sqrt{\alpha_s t} \quad (\text{S3})$$

where z is vertical distance from the cold plate, t is time, T_{Hot} and T_{Cold} are the boundary temperatures, T_m is the liquid melting temperature, α is thermal diffusivity, and $\nu = \sqrt{\alpha_s/\alpha_l}$. Λ is a dimensionless parameter solved using a transcendental equation:

$$\Lambda\sqrt{\pi} = \frac{St_s}{\exp(\Lambda^2) \operatorname{erf}(\Lambda)} - \frac{St_l}{\mu\nu \exp(\mu^2\nu^2\Lambda^2) \operatorname{erfc}(\mu\nu\Lambda)} \quad (\text{S4})$$

where $St_s = c_p^s(T_m - T_{Cold})/L$, $St_l = c_p^l(T_{Hot} - T_m)/L$, $\mu = \rho_s/\rho_l$, and $\alpha = k/\rho c$.

Subscripts l and s indicate the liquid or solid phases, respectively. Equation S4 depends on the boundary temperatures, T_{Hot} and T_{Cold} , the melting temperature, T_m , and the thermal and physical properties of the material frozen, specifically density, ρ , thermal conductivity, k , heat capacity, c_p , and the latent heat of fusion, L . The ratio μ is included in Equation S4 to account for the

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4 difference in density between the solid and the liquid. For the experimental setup described in
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6 section 2.1.2, T_{Hot} is the slurry temperature and T_{Cold} is temperature of the thermoelectric cooler.
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9 Velocity of the freezing front over time, $V(t)$, is obtained by taking the first derivative of the
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11 interface position (Equation S3):
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$$V(t) = \Lambda \sqrt{\alpha_s/t} \quad (S5)$$

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17 The magnitude of Λ is an indication of relative velocities for varying materials and problem
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19 setups.
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22 Several assumptions are made in the Neumann solution of the TPSP: (i) boundary
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24 temperatures (T_{Hot} , T_{Cold}) and freezing temperature (T_m) remain constant throughout freezing; (ii)
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26 the material being frozen is in the form of a semi-infinite slab; (iii) there is no undercooling in
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28 the system; (iv) the freezing front interface has zero thickness; and (v) the densities, heat
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30 capacities, and thermal conductivities of the individual phases do not change with temperature
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32 during solidification. Temperature of the TEC was monitored and adjusted *in situ* to ensure that
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34 T_{Cold} remained constant. Decreases in melting temperature due to slurry additives and the
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36 presence of ceramic particles is assumed to be minimal. The remaining assumptions, (ii) through
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38 (v), are adopted for simplicity and/or to allow for an explicit solution to the problem for all
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Table 1

Table 1: Summary of freezing parameters used for casting water- and camphene-based samples

where T_{Hot} is the temperature of the slurry before casting and T_{Cold} is the temperature of the TEC.

Also included are measurements for lamellar spacing (λ) and pore width (w) for water-based samples, pore diameter (d) for camphene-based samples, and geometric surface area (GSA) and tortuosity (τ) for all samples.

<i>Dispersion</i>	T_{Hot}	T_{Cold}	<i>Lamellar</i>	<i>Pore Width,</i>	<i>Geometric Surface</i>	<i>Tortuosity,</i>
<i>Medium</i>	(°C)	(°C)	<i>Spacing, λ (μm)</i>	<i>w (μm)</i>	<i>Area, GSA (cm^2/cm^3)</i>	<i>τ (cm/cm)</i>
Water	10	-15	54.9	32.9	362	1.1
	15	-20	52.5	31.2	650	1.1
	15	-45	45.5	25.8	645	1.1
	25	-10	78.1	49.5	544	1.1
	25	-20	53.3	31.9	675	1.1
	25	-30	53.3	31.7	879	1.1
	30	-35	43.1	24.3	619	1.1
	35	-20	62.3	37.6	880	1.1
Camphene	T_{Hot}	T_{Cold}	<i>Pore Diameter,</i>		<i>Geometric Surface</i>	<i>Tortuosity,</i>
	(°C)	(°C)	<i>d (μm)</i>		<i>Area, GSA (cm^2/cm^3)</i>	<i>τ (cm/cm)</i>
	50	15	40.8		821	1.5
	60	25	54.9		1028	1.4
	60	15	38.9		1212	1.4
	60	5	33.2		1023	1.4
	60	-5	31.1		1160	1.3
	70	15	37.0		1341	1.3

Table 2

Table 2: List of thermal property values for pure substances and slurries at the maximum T_{Hot} and minimum T_{Cold} for each type of sample. Values were obtained from the literature for pure dispersion media or were calculated for slurries using the methods described. Camphene used was >78% pure (–)-camphene with ~ 2% isomers, primarily α -fenchene, and a remainder of other unidentified tricyclene isomers of camphene and minor impurities. Due to the limited data available for this mixture, many properties are for pure (–)-camphene or 95-100% ($\pm$)-camphene, and are indicated with superscripts, (–) for (–)-camphene or ($\pm$) for ($\pm$)-camphene. Values for the exact camphene used do not have superscripts.

	Water		Camphene	
	Liquid	Solid	Liquid	Solid
Property	$T_{Hot} = 35^{\circ}C$	$T_{Cold} = -45^{\circ}C$	$T_{Hot} = 70^{\circ}C$	$T_{Cold} = 5^{\circ}C$
T_m ($^{\circ}C$)	0 [56]		$35^{(-)}$ [19]	
ρ (g/cm^3)	0.994 [41]	0.923 [56]	$0.803^{(-)}$ [46]	0.850 [19]
c_p ($J/g\cdot K$)	4.18 [41]	1.77 [56]	$1.92^{(\pm)}$ [48]	$1.59^{(\pm)}$ [48]
k ($W/m\cdot K$)	0.623 [41]	2.69 [56]	$0.103^{(-)}$ [45]	$0.12^{(\pm)}$ [47]
L (J/g)	333 [56]		$19.8^{(\pm)}$ [48]	
Calculated Slurry Properties				
ρ_{slurry} (g/cm^3)	1.690	1.635	1.515	1.551
$c_{p_{slurry}}$ ($J/g\cdot K$)	2.58	1.32	1.51	1.28
k_{slurry} ($W/m\cdot K$)	1.16	18.6	0.192	11.2
L_{slurry} (J/g)	150		8.1	

Table 3: Regression models for pore size and lamellar spacing as functions of $\Lambda_{dm/slurry}$ or $\Lambda_{dm/slurry}$ and G_{app} .

$\Lambda = \Lambda_{dm}$				
Dispersion	Regression	Exponents	Model	Model
Medium	Model	(n, m)	P-values	Adj. R-sq.
Water	$\lambda_w \propto \Lambda^{-n}$	0.69 ± 0.24	0.001	81.8%
	$w_w \propto \Lambda^{-n}$	0.84 ± 0.27	0.001	83.2%
Camphene	$d_c \propto \Lambda^{-n} G_{app}^{-m}$	$0.41 \pm 0.10,$ 0.33 ± 0.09	0.001	98.1%
$\Lambda = \Lambda_{slurry}$				
Dispersion	Regression	Exponents	Model	Model
Medium	Model	(n, m)	P-values	Adj. R-sq.
Water	$\lambda_w \propto \Lambda^{-n}$	0.73 ± 0.26	0.001	81.1%
	$w_w \propto \Lambda^{-n}$	0.89 ± 0.30	0.001	82.6%
Camphene	$d_c \propto \Lambda^{-n} G_{app}^{-m}$	$0.57 \pm 0.15,$ 0.34 ± 0.09	0.002	97.7%

Table 4: Regression models for GSA as functions of $\Lambda_{dm/slurry}$ or $\Lambda_{dm/slurry}$ and G_{app} , where GSA is sample surface area normalized by total pore volume.

$\Lambda = \Lambda_{dm}$				
Dispersion	Regression	Exponents	Model	Model
Medium	Model	(n, m)	P-values	Adj. R-sq.
Water	$GSA \propto \Lambda^n$	1.09 ± 0.32	0.001	86.2%
Camphene	$GSA \propto \Lambda^n G_{app}^m$	$0.31 \pm 0.05,$ 0.32 ± 0.04	< 0.001	99.5%
$\Lambda = \Lambda_{slurry}$				
Dispersion	Regression	Exponents	Model	Model
Medium	Model	(n, m)	P-values	Adj. R-sq.
Water	$GSA \propto \Lambda^n$	1.15 ± 0.34	0.001	85.7%
Camphene	$GSA \propto \Lambda^n G_{app}^m$	$0.43 \pm 0.05,$ 0.33 ± 0.03	< 0.001	99.6%

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure Captions

Figure 1: Schematic of directional freeze casting, adapted from Deville.[3]

Figure 2: Schematic of the freeze casting setup.

Figure 3: Schematic defining tortuosity between points A and B. The thick solid line is the geodesic length of the pore centerline, L , and the dashed line is the Euclidean length of the pore, R . [28]

Figure 4: Water-based samples (a) parallel (SEM) and (c) perpendicular (XCT) to the freezing direction, and (e) a 3D XCT reconstruction. Camphene-based samples (b) parallel (SEM) and (d) perpendicular (XCT) to the freezing direction, and (g) a 3D XCT reconstruction. **Images (a) through (d) are of epoxy-filled samples.**

Figure 5: Graphical representations of the regression models in **Error! Reference source not found.** for (a) lamellar spacing and (b) pore width for water-based samples for both A_{dm} and A_{slurry} , and of the regression models for camphene-based samples versus (c) A_{dm} and G_{app} , and (d) A_{slurry} and G_{app} . The contours in (c) and (d) correspond to pore diameter values.

Figure 6: Graphs of geometric surface area regression models from **Error! Reference source not found.** for (a) water-based, and (b) and (c) camphene-based samples using (b) A_{dm} and G_{app} , and (c) A_{slurry} and G_{app} . Contours in (b) and (c) correspond to measured geometric surface area.

Figure S1: Schematic describing the two-phase Stefan problem.