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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. Classical 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 primarily on the type of dispersion medium.

Keywords: Freeze casting; Porous ceramics; Directional solidification; X-ray computed tomography; Modeling

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 Fig. 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 [4,5,6,7,8]. 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 [3,5,9,10,11].

In addition to porosity and pore size, other pore network characteristics such as pore morphology, tortuosity, and 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, camphene-based slurries result in dendritic pores, and *tert*-butyl alcohol-based samples have prismatic pores [3,14]. Dispersion media themselves can also be altered by inclusion of additives designed to alter the freezing temperature, pH,

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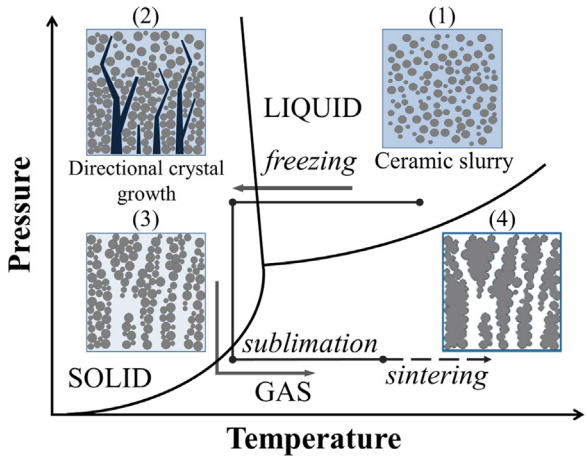

Fig. 1. Schematic of directional freeze casting, adapted from Deville [3].

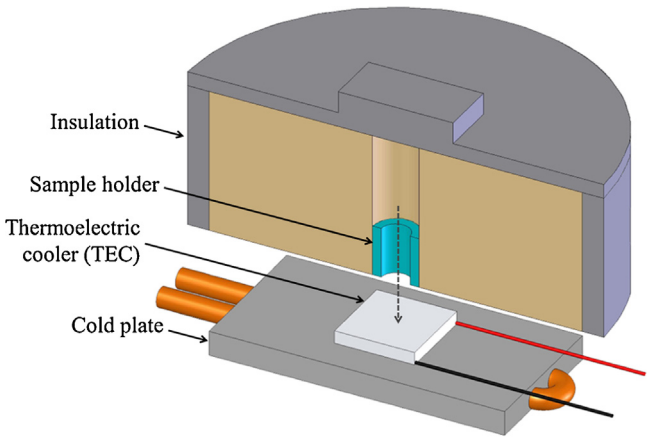

Fig. 2. Schematic of the freeze casting setup.

or viscosity of the liquid [3]. Control over surface area and tortuosity has not been established or well-studied.

The ability to use freeze-cast products commercially requires easy fabrication and increase in production scale. If small-scale freeze casting is considered as a volume element of a large scale production process, the ability to predict pore network characteristics without iterative testing in a specially designed casting setup becomes possible. As such, the overarching purpose of this study is to describe the development of and results for freeze casting models that will allow researchers to determine processing conditions required to yield a set of pore network characteristics a priori. Since pore size in freeze-cast samples is reportedly influenced by freezing front velocity, a pore size model must include a method of predicting freezing front velocity from freezing conditions, a requirement that will be satisfied using the two-phase Stefan problem. Traditional solidification theory will subsequently be used to describe relationships between feature size and freezing conditions. The two parts are then combined and applied to freeze casting. Pore size data measured from freeze-cast samples will be presented and used in development of the model. Pore size models are then extended to geometric surface area and tortuosity using morphological considerations, and validated using the data collected.

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 h 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 h to remove the solidified dispersion medium. Camphene-based castings were left in a fume hood at ambient conditions for the same period [16,17,18]. No sample deformation was observed during the drying stage for either type of sample. Finally, samples were sintered at 1600 °C for 5 h 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 Fig. 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