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# Influence of anisotropic grains (platelets) on the microstructure and uniaxial compressive response of ice-templated sintered alumina scaffolds

Dipankar Ghosh*, Hyungsuk Kang, Mahesh Banda, Valere Kamaha

*Department of Mechanical and Aerospace Engineering, Old Dominion University, Norfolk, VA, 23529, USA*

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ABSTRACT

Ice-templated ceramics have unique lamellar pore morphology that offers better compressive mechanical properties in comparison to the typical ceramic foams with isotropic pore morphology. However, for very high-level porosity (>65 vol%) strength difference diminishes. This investigation reveals that by inducing anisotropic grains within the matrix of a fine-grained ceramic, uniaxial compressive response of the ice-templated sintered scaffolds can be markedly enhanced without causing any considerable modification of the total porosity. To address this innovative materials design strategy, we synthesized a series of microstructures by systematically varying the anisotropic grains content in an aqueous suspension and the freezing kinetics to investigate the process-microstructure correlations and understand the structure-property relationships. Microstructural investigations revealed the unique arrangements of the platelets within and out of the lamella walls, where the upward moving ice fronts aligned the platelets' in-plane direction to the ice-growth direction. In the low freezing front velocity regime, platelets were observed to be mainly within the lamella walls, whereas platelets started to develop lamellar bridges with the increasing velocity. As a result, a transition of the pore morphology occurred with the increasing platelets content and the freezing front velocity. A novel method based on the rigorous microstructural analysis is developed to estimate the distribution of the platelets within and out of the walls and the variation of the platelets distribution with the composition and freezing front velocity. A drastic improvement of the compressive mechanical properties (stiffness, strength, energy absorption capacity) was measured due to the platelets' addition, which has been related to the platelets' distribution within and out of the walls and the pore morphology modifications. Results are rationalized based on the role of the platelets during the compressive deformation.



## 1. Introduction

Macroporous ceramic scaffolds with an oriented pore morphology and low pore tortuosity are an emerging class of materials that are promising for bone-tissue engineering, solid-state battery electrodes, solid oxide fuel cells, and impact energy-absorption. While the conventional ceramic foaming techniques yield isotropic pore morphology, freeze casting (also called ice-templating) is one technique that can synthesize ceramic scaffolds with oriented pores [1–8]. Structure-property (mechanical in particular) relationships of the ice-templated ceramics are not well understood, however, a limited number of studies suggest that relative density, lamellar bridge density, pore size, and lamella wall thickness are influencing factors to the uniaxial compressive response [1–3,6–9]. Relative density (thus total porosity) depends on the solids loading of a suspension, whereas the bridge density, pore size and wall thickness can be manipulated by exploiting the solids loading and the unidirectional freezing kinetics. Very little, however, is known about the influence of the anisotropic grains (e.g., ceramic platelets) on the compressive response of the ice-templated sintered ceramic scaffolds. Hunger et al. [10,11] showed that presence of large spherical or platelet $Al_2O_3$ particles in chitosan-alumina ($Al_2O_3$) freeze-cast porous composites reduced the lamella wall porosity and thereby improved the overall mechanical performance. However, there is no study that addresses the grain anisotropy effects on the mechanical response of the ice-

* Corresponding author.
*E-mail address:* dghosh@odu.edu (D. Ghosh).

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templated sintered scaffolds containing only the ceramic phase. To that end, the authors recently reported that $Al_2O_3$ platelets (diameter ~8 μm thickness ~400 nm) drastically improved compressive stiffness and fracture strength of the ice-templated highly porous (~80 vol%) sintered $Al_2O_3$ scaffolds that were mainly comprised of the equiaxed fine grains (1–3 μm) [12]. However, to develop the process-structure-property (mechanical) correlations of the newly developed novel platelets-reinforced ice-templated sintered porous scaffolds, it is imperative to conduct a study that systematically investigates the combined effects of the platelets content and the freezing kinetics, and addresses the interlinks in between the microstructural parameters and the mechanical response.

During an ice-templating process, particles are ejected by the upward moving ice fronts (under the influence of an unidirectional temperature gradient) and accumulate in between the growing ice lamellae [3]. Presence of large anisotropic platelets in an aqueous suspension containing mainly equiaxed fine particles and variation of the platelets fraction are expected to affect the particle packing during the freeze casting and the densification during sintering. This is because while a small amount of platelets in a matrix of equiaxed fine particles can improve the packing fraction and densification, both may deteriorate with the increasing platelets concentration. It is thus possible that strength of the sintered scaffolds may go through a maximum. Another consideration is that pore morphology of the ice-templated scaffolds gradually transitions from lamellar to dendritic to isotropic structure with the increasing particle size [13,14]. Since, lamellar bridge density and pore size increases and decreases, respectively, with the transition of the pore architecture from lamellar to dendritic to isotropic, strength of the scaffolds is expected to increase with the increasing particle size [14]. Therefore, increasing the fraction of the large platelets in a suspension containing fine equiaxed particles may cause a pore morphology transition from lamellar to dendritic/isotropic, resulting in a strength improvement. Moreover, freezing kinetics significantly influence the microstructure and mechanical response of the ice-templated scaffolds. Therefore, there could be competing factors that evolve with the change of the anisotropic grains (platelets) concentration and freezing kinetics and can influence the compressive response.

Therefore, this work synthesized ice-templated sintered porous $Al_2O_3$ scaffolds from the equiaxed fine particles as well as from the mixtures of the equiaxed fine and large platelet particles. Microstructural evolution was characterized as a function of the anisotropic grains content and the freezing front velocity (FFV). And the observed changes of the relative density and microstructure were linked to the measured uniaxial compressive mechanical response to understand the effects of the grain-level anisotropy on the structure-property (mechanical) relationships.

## 2. Experimental

### 2.1. Materials and aqueous ceramic suspension preparation

Ice-templated scaffolds were processed from the commercially available fine equiaxed $Al_2O_3$ powder (~0.9 μm, Alfa Aesar, Ward Hill, MA) and large $Al_2O_3$ platelets (diameter ~8 μm and thickness ~400 nm, Alusion™, Antaria Ltd., Bentley, Western Australia); referred to here as SA and PA, respectively. All the scaffolds were processed from aqueous suspensions with 15 vol% $Al_2O_3$ content. However, within the 15 vol% of total $Al_2O_3$ content, proportion of the SA and PA was varied and scaffolds were synthesized from five different compositions: (i) SA (0 vol% PA), (ii) SA-2.5PA (2.5 vol% PA), (iii) SA-5PA (5 vol% PA), (iv) SA-10PA (10 vol% PA), and (v) SA-20PA (20 vol% PA). Here, PA content is presented with respect to the total $Al_2O_3$ content.

### 2.2. Unidirectional freeze casting and sintering

A custom-made device was employed to conduct the unidirectional ice-templating experiments [14]. In this device, by adjusting the gap in between the cold-finger and the liquid $N_2$ (L-$N_2$) surface unidirectional thermal gradient and thus the FFV are controlled, where the FFV increases with the decreasing gap. Distance in between the cold finger and the L-$N_2$ surface was kept fixed during a freeze casting experiment. However, the gap was varied from scaffold to scaffold to change the average FFV. Minimum and maximum gaps used were 1 mm and 30 mm, respectively. Ice-templated $Al_2O_3$ scaffolds were processed within an FFV (average) range of ~10–35 μm/s. For each experiment, an average FFV is estimated by dividing the height of a frozen sample with the time required for completion of solidification of the suspension. Samples were next freeze-dried at a low pressure 0.014 mbar and temperature −50 °C for 96 h and sintered at 1550 °C for 4 h.

### 2.3. Microstructure characterization, density measurements and uniaxial compression testing

Although the sintered scaffolds were about 16.5 mm in diameter and of 39 mm height, a small sample was extracted from each scaffold (Fig. S1) for the microstructural characterization, density measurement, and compression test. For the microstructural characterization, a transverse plane (top plane) of each specimen was utilized (Fig. S1). Sintered density of each specimen ($\rho^*$) was determined from the mass and dimensions. Relative density ($\rho_r$) was estimated using $\rho_r = \rho^*/\rho_s$, where $\rho_s$ is the bulk density of α-$Al_2O_3$ (3.96 g/cm$^3$). Total porosity was estimated using $p_t = (1 - \rho_r) \times 100$. A Tinius Olsen (model 10ST) mechanical testing machine equipped with a 5 kN load cell was employed to conduct the uniaxial compression experiments using a displacement rate of 0.5 mm/min. More details of the experiments are available in the Supplementary material.

## 3. Results

### 3.1. Microstructure evolution with platelets content and freezing front velocity

Fig. 1 shows the representative microstructures of all the sintered porous scaffolds at relatively low and high FFVs, where each SEM micrograph corresponds to the transverse plane (top plane) located at a height of 9 mm from the bottom of a sintered cylindrical scaffold (Fig. S1). Fig. S2a and S2b reveal microstructures of the top plane (located at 9 mm from the bottom) and bottom plane (located at 5 mm from the bottom), respectively, of a specimen extracted from the sintered SA scaffold processed at a relatively low FFV (16.9 μm/s). Both planes exhibit comparable microstructures, suggesting negligible microstructural variations within a distance of 4 mm along the ice-growth direction. Therefore, the SEM micrographs corresponding to the top planes (Fig. 1) can be considered as the representative of the overall microstructures of the small rectangular specimens, utilized for the density measurements and uniaxial compression tests. For all the compositions, pore morphology of the sintered scaffolds at low FFVs could be considered as lamellar. However, at high FFVs pore morphology of the scaffolds appears to be dendritic due to the increased lamellar bridges. Moreover, extent of the lamellar bridging at high FFVs also appears to increase with the PA content. Fig. 2a and 2b show the microstructural variations of the SA and SA-20PA, respectively, with