Tunable Compressive Mechanical Behavior of Ice-Templated Materials

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TUNABLE COMPRESSIVE MECHANICAL BEHAVIOR OF
ICE-TEMPLATED MATERIALS

by

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ABSTRACT

TUNABLE COMPRESSIVE MECHANICAL BEHAVIOR OF ICE-TEMPLATED MATERIALS

Sashanka Akurati
Old Dominion University, 2021
Director: Dr. Dr. Dipankar Ghosh

The inherent hierarchical microstructural organization in natural materials is responsible for their excellent mechanical properties beyond that predicted by the simple rule-of-mixtures. Further exhibit synergy between strength and toughness, otherwise mutually exclusive in brittle materials. Conventional processing methods are unable to replicate hierarchical microstructures in engineering ceramics akin to that observed in natural materials. Ice-templating has emerged as a potential technique to fabricate bioinspired hierarchical materials. This process involves simultaneous unidirectional solidification and phase segregation of aqueous suspensions. Ice-templated porous ceramic materials have received significant attention for overcoming several limitations of conventional ceramic foams currently used in numerous engineering applications.

The purpose of this dissertation is many-folds with a central theme of tunable compressive response, which has been revealed by investigating microstructure-mechanical property relationships in both ice-templated ceramics and infiltrated composites.

First, this dissertation developed a novel extrinsic methodology. The alternating current (AC) electric field was uniquely employed to tailor ice-templated microstructure and mechanical properties. This research revealed that local suspension concentration could be effectively manipulated by applying AC electric fields to aqueous ceramic suspensions, providing a novel approach to tune ice-templated microstructure and remarkably enhance compressive mechanical properties without compromising porosity.
Next, this dissertation investigated the loading orientation dependence of the compressive response of freeze cast ceramic-polymer composites, motivated by the structural gradient observed in natural materials. The results revealed a strong orientation dependence of compressive response and failure behavior (catastrophic vs. progressive). Furthermore, this dissertation investigated inelastic deformation mechanisms that evolve in these composites under compressive loading conditions and cause macroscopic failure. It was revealed that the deformation mechanisms were also strongly influenced by the loading orientation.

Finally, this dissertation investigated compressive response and damage evolution in ice-templated ceramics and composites under high-strain rate (dynamic) loading conditions. Ice-templated materials with higher porosity exhibited progressive crushing type damage evolution, irrespective of the strain rate regime. The results suggested greater structural stability in ice-templated ceramics at high-strain rates. This dissertation also investigated the influence of microstructure on the impact behavior of ice-templated sintered alumina materials and the relationship between dynamic compressive strength and impact response.
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This dissertation is dedicated to my family & friends.
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CHAPTER 1

INTRODUCTION

1.1 Natural materials for bioinspired materials design

Natural materials are composed of a limited number of components that have poor intrinsic mechanical properties [1–4]. After millions of years, natural materials evolved to exhibit exceptional mechanical properties that far exceed their material constituents [2]. There is a strong interest in bioinspired materials design for engineering materials with improved mechanical and functional properties. Natural materials provide major bioinspiration for lightweight, flexible, strong, and tough [2,5]. On the contrary, strong materials are often brittle, while tough materials are low in strength. For a long time, nature has solved the classic materials-design problem of combining two mutually exclusive structural properties [3,4,6].

The natural materials are often hybrid composites made up of hard and soft phases formed from a limited number of weak constituents as building blocks. The building blocks are grouped into four classes: (a) ceramics and ceramic composites, (b) polymers and polymer composites, (c) cellular, and (d) elastomers [3]. Figure 1a denotes the material properties map signifying the toughness and Young’s modulus for the building blocks found in all natural materials. Natural elastomers (soft phase) are located on the upper left, exhibit high toughness. While natural ceramics, i.e., the mineralized components (hard phase) on the lower right, exhibit high stiffness. The natural hybrid composites (bone, seashells, teeth) have efficiently incorporated natural ceramic and polymer components resulting in synergy between stiffness and toughness. Figure 1b considers two natural mineralized composites, bone and nacre. These materials are composed of weak individual constituents; however, the mechanical properties of these composites far exceed
those of their material constituents, and that is predicted by simple rule-of-mixtures [2]. To this end, the mechanical properties exhibited by natural materials are not primarily a function of the material constituents. However, the structure and arrangement of constituents dictate exceptional mechanical properties [2,3]. The origin of superior properties in natural hybrid materials is inherently related to the hierarchical organization of components encompassing multiple length scales [4]. There is a substantial interest in achieving enhanced mechanical and functional properties in engineering materials. A future composite fabricated from advanced engineering materials and nature-inspired strategies may likely result in exceptionally high toughness, Figure 1b.

**Figure 1:** (a) Material properties map for natural materials plotting toughness and Young’s modulus [3]. (b) The toughness values of natural composite materials (bone and nacre) far exceed those predicted by the rule of mixtures. Adapted with permission from [2].

However, a limited number of material constituents have developed similar solutions to address specific environmental constraints [2,3]. The most common structural design elements in
natural materials are fibrous, helical, tubular, cellular, suture, overlapping, gradient, and layered
[7]. These structural elements have evolved to improve the mechanical properties, namely strength,
stiffness, flexibility, fracture toughness, wear resistance, energy absorption, and functional
properties [2,4,7]. Discussions in the following sections are limited to layered architecture and
structural gradient, describing their mechanical and structural advantages.

1.1.1 Multilayered architecture

The high mineral content in natural hybrid composites (nacre, skeleton of sponge, bones),
as shown previously in Figure 1a, should be expected to be brittle. However, exhibit enhanced
toughness magnitudes higher than its components. Natural composites have evolved to increase the
toughness by introducing interfaces by adopting layered architecture with alternate layers of hard
and soft phases [2,7]. Figure 2a shows multilayered hierarchical organization in nacre, consisting
of 95 vol% of inorganic (aragonite) layers glued together by 5 vol.% of organic (biopolymer)
phase. Nacre (mother of pearl) is a high-performance material often found on the inner layers of
abalone seashells. It offers protection to the soft organism (mollusk) against attacks from predators,
debris, and rocks.

Furthermore, nacre is one of the most investigated natural materials to understand its
mechanical properties and deformation mechanisms. Nacre relatively exhibits a lower compressive
strength in the loading direction parallel (θ = 0°) to layer orientation compared to the perpendicular
(θ = 90°) direction. According to Menig et al. [8], compressive strength in perpendicular direction
was about 50% higher compared to parallel direction. Also, nacre exhibited higher failure strains
in the stronger direction, i.e., compression perpendicular to layer orientation. Menig et al. [8]
described loading nacre in the perpendicular direction led to deflection of cracks. The weaker
organic phase, i.e., the viscoelastic layers, allowed the sliding of CaCO₃ platelets to incorporate
more significant deformations. In contrast, nacre on loading in the parallel direction exhibited vertical splitting and deformed inelastically by the formation of kink bands caused by plastic micro buckling, Figure 2c, 2d [8,9]. Under bending loads, nacre propagates crack in a stable manner through tortuous crack paths (Figure 2b), exhibiting enhanced toughness, Figure 2e [5].

Figure 2: (a) Multilayered hierarchical structural organization in nacre. Adapted with permission from [2,10]. (b) The tortuous crack path was observed in the nacre. (c-d) Compressive strength anisotropy and probability of failure in nacre. Adapted with permission from [9]. (e) Load displacement signature for nacre under bending. Adapted with permission from [5].

1.1.2 Structural gradient

Another common design feature observed in natural materials is structural gradient. Adopting continuously varying structures through-thickness or cross-sections along the materials enables enhanced offensive and defensive mechanisms, resulting in graded mechanical properties [11]. Further,
this structural feature provides toughness, resist wear, or arrest crack growth [7]. Natural hybrids such as teeth, fish scales, pangolin scales, and lobster cuticles are some of the specific examples [2,4,12–15]. Pangolin, a type of armed mammal, exhibits the unique feature of overlapping scales covering most of their skin, as shown in Figure 3 (a). This scaly armored manner is proposed to enhance the flexibility of the pangolin compared to other reptiles and animals.

Moreover, these overlapping scales also help pangolins to protect themselves from predators. Liu et al. [16] extensively studied pangolin scales' deformation and fractured behavior and correlated them with the structure. In this study, pangolin scales were tested for hardness, tension, and compression in both dry and wet scales to understand the mechanical behavior. It shows three micro-layers layers, dorsal, intermediate, and ventral layers. All three layers exhibited lamellar structure, and lamellae in the dorsal region were oriented parallel to the outer surface at the topmost region. There is a trade-off between tensile strength and the tensile strain of biological materials along all three directions illustrated in Figure 3f. Wet samples under compression exhibited lower strength and lower modulus with notable strain-hardening by hydration. In wet samples, hardness was significantly decreased by hydration. The intermediate layer exhibited higher hardness in both dry and wet conditions on the longitudinal section than in the transverse one, Figure 3i. This trend is strongly associated with the orientation of lamellae in respective sections. This study demonstrated that materials that adopted structural gradients had enhanced strain hardening under contact loads, maximizing performance [16].
Figure 3: (a) Macroscopic optical image of pangolin and its scale. (b-c) The structural gradient was observed on a pangolin scale. (d-h) Tensile and compressive stress-strain responses both in dry and wet conditions. (i) Variation of hardness on the longitudinal and transverse sections. Adapted with permission from [16].

1.2 Bioinspired approach

The principles employed in hierarchical biological materials cannot be applied to the design of new engineering materials. Nature employs completely distinctive design strategies. The striking difference is found in the choice of base elements used in the construction of the materials. Secondly, the growth and fabrication paradigms used by nature and engineers respectively
establish the definitive difference in designing the materials. As seen in Figure 4, there are many materials to choose from for fabricating an engineering material, such as iron, chromium, nickel. These are seldom found in biological materials and certainly not metallic forms. Polymers, polymer composites, and ceramics (calcium carbonate) are utilized by nature, posing durability and longevity issues for an engineer. Nature overcomes the limitations imposed due to the chemical environment and adverse temperatures to build trees and skeletons using polymers and ceramics [4].

When it comes to the design strategy, an engineer follows a static way where functional prerequisites, future changes of those requirements, and failure or fatigue limitations are considered prior to the material design and fabrication. At the same time, nature employs a dynamic strategy of biologically controlled self-assembly, paving the way for the materials to be grown rather than fabricated. Therefore, despite having fewer materials to work with, the material development strategy of nature exerts control at all the hierarchical levels to successfully employ polymers and composites as structural materials [4].

However, a profound challenge is to develop suitable fabrication techniques that mimic the complex features of the hierarchical microstructure of natural composites into engineering materials. Toward this end, freeze-casting, also known as ice-templating, has emerged as a method for the fabrication of nacre-inspired multilayered architecture.
**Figure 4:** Biological and engineering materials are governed by a very different choice of base elements and a different mode of fabrication. This results in different strategies for materials choice and development [4,6].

### 1.3 Freeze casting technique

Freeze-casting, also called ice-templating when aqueous suspensions are used, is a simultaneous unidirectional solidification and phase segregation process—controlling the velocity of anisotropic growth of solvent crystals in ceramic suspensions [17]. During solidification results in unique directionally porous materials with hierarchical multilayered microstructure. Ice-templating consists of four significant steps when performed on aqueous ceramic suspensions (Figure 5a) [18,19]. It begins with preparing a stable ceramic suspension, a recipe stating the amount of solute, solvent, and other additives. Here, the solvent is usually deionized water (DI) and solute primarily being ceramic particles. Additives such as dispersants are included to prepare
a stable suspension. Also, water-soluble binders are mixed during suspension preparation, which dictates freeze-dried samples' strength (green body).

In the second step, aqueous ceramic suspensions are unidirectionally solidified. To achieve a controlled freezing condition, suspensions are filled on a Teflon tube and placed on the metal “Cold-finger.” The complete assembly is radially insulated to induce ice-nucleation only near the cold finger region. Here, the ice-crystals grow along the unidirectional temperature gradient. Freeze-casting being a physical process, ceramic particles are either rejected or entrapped during the nucleation and growth of ice crystals [5]. Ceramic particles rejected from the growing ice crystals accumulate between alternate ice crystals. The final frozen structure consists of alternate layers of packed ceramic particles and ice crystals oriented along the temperature gradient.

Further, the frozen samples are freeze-dried to eliminate the templated ice crystals by the sublimation process. At the end of the third step, the macroporous green body is ready to be sintered to impart strength by the final sintering step. In the last step, sintering is performed at elevated temperatures resulting in an ice-templated macroporous sintered ceramic sample.

A typical ice-templated sintered porous ceramic is shown in Figure 5b. The microstructure consists of randomly oriented ceramic walls in the plane perpendicular to the ice-growth direction. Multiple ice-nucleation sites lead to multiple domains. Each domain consists set of parallelly oriented walls. Similarly, on the plane parallel to ice-growth results in aligned pore channels along temperature gradient resulting in anisotropic pore architecture with low pore tortuosity. This technique enables the fabrication of anisotropic structures, resulting in material properties beneficial in various targeted applications [20].
Figure 5: (a) Schematic representation of the freeze casting/ice-templating process for aqueous ceramic suspensions [18,19]. (b) Micro- and macro-structures in a typical ice-templated sintered porous ceramic.
During solidification, particles either get entrapped or accumulate between two ice crystals. As previously mentioned, the resulting microstructure is dependent on the physical interactions between the moving ice-front and the suspended particles. Figure 6 shows that there exists a correlation between critical freezing front velocity ($v_{cr}$) and freezing front velocity (FFV), ($v$) of the suspension that dictates the final microstructure [20]. There exist two competing mechanisms, particle rejection and particle entrapment resulting from the interactions between ice-front and suspended particles. The dotted line in Figure 6 denotes the optimum $v$ required to achieve directionally porous lamellar morphology of dendritic morphology (connected lamellar walls). Excessively high or exceptionally low freezing rates result in isotropic (complete entrapment) or planar ice-front (complete rejection).

**Figure 6:** Interaction between moving ice-front and suspended particles during the ice-templating process. The dotted line denotes the favorable conditions for forming a lamellar structure [20].

### 1.3.1 Process control variables to modify microstructures

As discussed in the previous section, there exists a critical freezing front velocity ($v_{cr}$) that results in either particle entrapment or rejection can be manipulated chemically and physically by changing suspension constituents and freezing conditions [20,21]. There are several factors
effecting $v_{cr}$ such as particle morphology, suspension viscosity, solvent type, solid loading, and temperature [ref]. The $v_{cr}$ is expressed as [20–23]:

$$v_{cr} = \frac{\Delta \sigma d}{3\eta R} \left( \frac{a_0}{d} \right)^z.$$  \hspace{1cm} (1)

where $\Delta \sigma$ is the mean free energy of a particle, $a_0$ is the average intermolecular distance in the liquid film between the particle and the solid front, $d$ is the overall thickness of this film, $\eta$ is the slurry viscosity, $R$ is the particle radius, and $z$ is an exponent that ranges between 1 to 5. The above equation is based on a force criteria-based approach for particle rejection and engulfment, which considers all the forces that act on a particle facing a solidification front. Equation (1) has commonly described the relationship between particle size and $v_{cr}$ in the ice-templating process [21,24–27].

According to equation (1), $v_{cr}$ is inversely proportional to particle radius ($R$). Suspensions processed at comparable freezing conditions and solid loading by simply altering the particle size significantly impacted the pore morphology and mechanical stability [25,28]. Studies have demonstrated that changing a small percentage of equiaxed particles with anisotropic platelet-shaped particles increased the propensity for lamellar bridge formation. With the moving ice-front, the anisotropic particles were entrapped, forming bridges. In contrast, the equiaxed-shaped particles were rejected formed lamella walls [28].

Furthermore, $v_{cr}$ is inversely proportional to viscosity ($\eta$). Studies have shown that the viscosity of suspensions is affected by the inclusion of additives [27,29]. For a comparable freezing condition and solid loading, a change in viscosity directly influences the $v_{cr}$, a high $\eta$ results in lowering the $v_{cr}$, enhancing particle entrapment resulting in dendritic morphology. At the same time, lamellar morphology is attained by decreasing the viscosity. Studies have modified the $\eta$ of suspension by systematically varying the concentration of additives and p$H$ of the suspensions for
a bit of change in overall porosity. However, the resulting materials have exhibited notable changes in compressive mechanical properties [29].

Based on the discussions in the previous section, the $v_{cr}$ plays a major in dictating the final microstructure. We can modify the particle entrapment and rejection by deliberately altering the freezing front velocity (FFV), resulting in complex microstructures. Adopting low FFVs results in the formation of a lamellar structure due to favorable conditions for particle rejection [21,30]. An increase in FFVs results in lamellar structures formed from the rejected particles accumulated between ice crystals. In contrast, lamellar bridges are formed by entrapped particles [30].

During unidirectional ice-templating, heterogeneous ice nucleation is influenced by the concentration of nucleation sites, i.e., particle concentration or solid loading. At a comparable freezing condition, the microstructure of ice-templated materials becomes increasingly finer by increasing solid loading. A low solid loading suspension results in a lamellar morphology with long elongated ceramic walls with less connectivity. In comparison, a higher solid loading suspension results in increased connectivity, i.e., dendritic morphology. Figure 7 shows examples for the role of different process control variables on the final ice-templated microstructures.
1.3.2 External energy fields in particle manipulation

There is an emerging interest in employing external energy fields to manipulate the spatial distribution of particles during the ice-templating process. In recent years, extrinsic manipulation of ice-templated ceramic microstructure has been attempted using magnetic [32,33], acoustic [34], and direct current (DC) electric fields [35–37]. Most ceramic materials are non-magnetic or weakly magnetic. Therefore, iron oxide nanoparticles were used to magnetize ceramic particle surfaces and make the ceramics respond to the external magnetic field [33,38]. Several studies showed the potential of a magnetic field in improving the alignment of lamella walls, increasing lamellar bridge density, and enhancing mechanical properties. Application of static magnetic fields (0.12 T) perpendicular to the ice-growth direction in titania (TiO₂) suspensions mixed with iron oxide nanoparticles resulted in directional alignment of lamella walls [39]. In the applied magnetic field direction, the fabricated ice-templated titania (TiO₂) materials displayed more than twice the compressive strength and modulus than materials without a field. Frank et al. [33] used surface
magnetized alumina (Al₂O₃) particles and platelets to fabricate ice-templated Al₂O₃ materials to show the influence of particle size, aspect ratio, and composition for aggregation into chains in the direction of the magnetic field. Acoustic pressure waves resulted in alternating concentric dense/porous rings [34]. Next on implementing the ice-templating process resulted in porous titania (TiO₂) materials with alternating concentric dense/porous rings. Application of direct current (DC) electric field along the ice-growth direction resulted in dense/porous bi-layered ice-templated Al₂O₃ materials. The thickness of the dense region was dependent on applied field strength [40]. To this end, it is evident that multiple underlying factors, competing mechanisms, and external energy fields can dictate the final templated microstructure. They enabled the fabrication of complex hierarchical porous ceramics with different pore morphologies for potential targeted applications.

### 1.3.3 Ice-templated composites

Ice-templating results in anisotropic pore architectures with low pore tortuosity and enables ease of infiltration of secondary phase material (polymer or metal). The resulted materials exhibit multilayered architecture, referred to here as ice-templated composites. Recently developed advanced ice-templated composites include alumina (Al₂O₃)–poly(methyl methacrylate) (PMMA) [41], Al₂O₃–epoxy [42], silicon carbide (SiC)–PMMA [43], Al₂O₃–bulk metallic glass [44], and Al₂O₃–aluminum-silicon alloy (Al-12Si) [45]. As previously discussed, multilayered architecture in natural materials resulted in stable crack growth for enhanced toughness. Therefore, most of the studies on ice-templated composites were limited to the characterization of mechanical behavior under 3-point bend loading for flexural strength and fracture toughness measurements [2,41,46,47]. The remarkable rising $R$-curve behavior in Al₂O₃–PMMA composites implies a stable crack growth, and fracture resistance increases with the crack extension [2,41,46,47].
Further, microstructural analysis in a 3D volume revealed damage is distributed over large (millimeter scale) dimensions, i.e., implying multiple cracks in the entire volume [41,43]. Although few studies on the mechanical properties of ice-templated ceramic–polymer composites for other loading conditions, such as uniaxial compression [48–50], a lack of knowledge exists on the inelastic deformation mechanisms which evolve in these materials under compressive loading conditions.

1.4 Recent trends with ice-templating

Ice-templating initially gained attention for the fabrication of nacre-like composites [5]. Ice-templating emerged as a versatile technique with several process control variables (freezing agents, solid loading, and additives). Enabled fabrication of open-cell macroporous ceramics materials with unique pore architectures (lamellar, dendritic, cellular, honeycomb) [17,25,51]. To this end, ice-templating is a material independent process. Signifying any materials can be utilized for ice-templating process as long as a stable suspension can be processed. Recently several 1D and 2D building blocks (nanoparticles, nanotubes, nanowires, nanofibers, nanosheets, nanoplatelets, polymer chains, and macromolecules) were employed to fabricate porous materials [20]. Recent studies focused on obtaining physical and functional properties (Table 1) for various possible applications [52]. Furthermore, using different building blocks in the ice-templating process, Figure 8 illustrates the emerging applications associated with ice-templated materials (porous and dense) [20].
**Table 1:** Recent trend on the targeted application of ice-templated materials. Adapted with permission from [52].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Materials considered</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>Ceramics, polymers</td>
<td>Tissue engineering, filtration, membranes, thermal insulation, acoustic adsorption</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Ceramics, metals</td>
<td>Filtration, tissue engineering</td>
</tr>
<tr>
<td>Toughness</td>
<td>Ceramics, metal/ceramic composites</td>
<td>Armor, impact resistance, high-performance structural materials</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>Carbon, silica, alumina, titania, graphene, chitosan, nanocellulose</td>
<td>Catalysis, adsorption</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Carbon, cellulose, chitosan, graphene, graphene oxide, copper, clay, silica, collagen</td>
<td>Adsorption of gas and heavy ions</td>
</tr>
<tr>
<td>Permeability</td>
<td>Alumina, silicon carbide, silicon nitride, collagen</td>
<td>Filtration, catalysis</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Graphene, carbon nanotubes</td>
<td>Batteries, supercapacitors, sensors</td>
</tr>
<tr>
<td>Dielectric properties</td>
<td>Silicon nitride, SiAlON, lead zirconate, rare-earth silicate</td>
<td>Microelectronics</td>
</tr>
<tr>
<td>Piezoelectric properties</td>
<td>Barium titanate, PZT, PZN</td>
<td></td>
</tr>
<tr>
<td>Capacitance</td>
<td>Graphene, graphene oxide, carbon nanotubes, barium titanate</td>
<td>Batteries, supercapacitors</td>
</tr>
<tr>
<td>Permittivity</td>
<td>PZT, barium titanate</td>
<td>Dielectrics, microelectronics</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Silica, rare-earth silicate, alumina, zirconia, silicon nitride, mullite, clay, carbon nanotubes</td>
<td>Thermal insulation, flame retardancy, thermal energy storage</td>
</tr>
</tbody>
</table>
1.5 High-strain rate behavior of materials

Strain rate is defined as the rate of deformation, which is the ratio of deformation in material and the duration of the applied load. For a comparable deformation in a material, loads are applied for longer durations under low-strain rates (quasistatic), resulting in strain rates between $10^{-5}$ s$^{-1}$ to $10^{-2}$ s$^{-1}$. While at high-strain rates (dynamic) ($>10^2$ s$^{-1}$), similar loads are applied for a short span. Most engineering materials exhibit strain rates dependent on mechanical deformation behavior and failure [53]. For engineering materials employed in different challenging environments, it is essential to understand the mechanical behavior and failure characteristics in quasistatic and dynamic loading conditions.

The typical characteristics observed in materials when the loading conditions transition from quasistatic to dynamic are [53] (i) deformation behavior transitions from ductile to brittle, (ii) inertial effects come into existence, (iii) induces severe fragmentation, and (iv) generated stress
waves propagate and initiate damage away from the location of the applied load. However, the above characteristics material behavior is generalized. Therefore, there is a need to understand each specific material system and can only be verified experimentally. The inelastic failure mechanisms are dependent on microstructural features, defects, loading type, stress state, sample geometry, and design parameters [54]. Further, damage evolution in ceramic materials is complex under dynamic loading conditions. Therefore, the deformation mechanisms should also be considered in addition to evaluating material properties (strength, hardness, and density) [53]. To this end, the mechanical properties of materials evaluated under quasistatic loading do not truly represent their mechanical behavior under dynamic loading [55]. Therefore, there is a strong interest in exploring the mechanical properties at different loading rates.

1.6 Research scope

1.6.1 Use of alternating current (AC) electric fields

As previously discussed, there is an emerging interest in combining external energy fields to manipulate the spatial distribution of particles during ice templating. To this end, external energy field-assisted fabrication of ice-templated ceramics was achieved using magnetic, acoustic, direct current (DC) energy fields. Employing advanced ceramics such as alumina (Al₂O₃), zirconia (ZrO₂), barium titanate (BaTiO₃), and titania (TiO₂) which are non-magnetic or weakly respond to magnetic fields. Studies have demonstrated using iron oxide nanoparticles to magnetize ceramic particle surfaces [ref]. On the other hand, studies employing acoustic fields achieved acoustic orientation only in low solid loading ceramic suspensions. There is a need to explore an alternative energy field that can be employed without the need for a secondary phase and is feasible for a wide range of solid loading.
While applying an external electric field to particle suspensions, two phenomena can occur, i.e., (i) electrophoresis and (ii) dielectrophoresis (DEP) [56]. Electrophoresis is the translational motion of charged matter within an electric field. Application of DC electric fields to ceramic suspensions has been demonstrated in varying the thickness of dense regions by electrophoretic deposition based on electrophoresis. While DEP can be observed both in AC and DC fields, particle migration is caused by the induction of polarization in non-uniform electric fields [57]. The significant difference between the above two phenomena is that DEP force depends not on the sign of the applied electric field or the charge on the particle surface. At the same time, the electrophoresis is dependent on both applied field direction and the sign of particle charge. Next, the DEP is proportional to the particle volume, and electrophoresis depends on particle size. Finally, DEP forces act only in the presence of wildly divergent non-uniform electric fields. At the same time, electrophoresis is observed both in uniform and non-uniform fields. In the presence of high solid loading, DEP forces act upon particles to attract each other and agglomerate as chains in the direction of the applied electric field [58–61].

Application of an alternating current (AC) electric field to a media containing particles of electrical properties (permittivity and conductivity) different than the media causes electric field nonuniformity [60]. The particles in the media experience frequency-dependent polarization, and the interactions of the induced dipoles with the non-uniform electric field result in the DEP forces, which cause particle motion and interparticle interactions. AC electric fields can be created and controlled at large spatial scales. The only necessary condition for AC field-induced interparticle interactions is a contrast between the complex dielectric permittivity of the particle and solvent. While DEP forces have been used for the manipulation of polymeric particles, metallic
nanoparticles, live cells, DNA, and carbon nanotubes (CNTs) [62–66], such studies are sparse for advanced ceramic material particles in aqueous media [67].

AC electric fields in combination with ice-templating have potential application as one provides a directed assembly of ceramic particles in an aqueous medium into (particle chaining) structures. At the same time, the latter plays an essential role in inducing a porous structure. A thorough understanding of this combined phenomenon in manipulating particles includes the parametric study on the effect of applied AC field strength, AC frequency, field duration, solid loading, particle size, and freezing rates.

1.6.2 High-strain rate behavior of ice-templated materials

As previously discussed, it is crucial to understand the deformation response of materials at different loading rates. Recent studies have demonstrated the effect of porosity, solid loading on the mechanical properties under quasistatic and dynamic loads for ice-templated porous materials processed at a comparable FFV [55,68]. To this end, there is minimal understanding of the damage evolution process in correlations to porosity, ice-templated microstructure, and strain rate. Also, there is no available design guideline to synthesize ice-templated porous ceramics of targeted porosity and microstructure concerning desired mechanical performance under dynamic and quasistatic compressive loading conditions.

On the other hand, ice-templated porous ceramics can be infiltrated with a polymer phase to fabricate dense (non-porous) multilayered ceramic-polymer composites. It is known that both the ceramic (alumina) and polymer (epoxy) exhibit strain rate dependence on the compressive mechanical properties [69–72]. However, there is minimal understanding of the high-strain rate behavior of ice-templated ceramic-polymer composites. Multiple factors need to be considered to perform a systematic study, such as solid loading, pore morphology, and freezing rates. Therefore,
to understand the loading rate effects, the uniaxial compressive response of ice-templated porous ceramic, pure polymer phase, and infiltrated composites must be explored.

1.6.3 Role of loading direction and deformation mechanisms

A structural gradient in a multilayered architecture is one of the prominent features observed in natural materials enabling gradient in mechanical properties [7]. Under contact loads from predators, the outermost regions in these structurally gradient materials respond differently than interior regions [2,3,11]. There is a substantial interest in fabricating complex architectures and envisioning graded mechanical properties to engineering materials. However, there is a limited understanding of the fundamental microstructure mechanical property correlations at different loading orientations. It is important to note that fabricating materials with complex hierarchical architectures is still premature. With recent progress on the fabrication of ice-templated ceramic-polymer composites, there is limited knowledge on the underlying uniaxial compressive deformation mechanisms under compressive loads. There is a need to predict the compressive strength for different material systems to progress ice-templating materials for application on a large scale. To this end, there is limited knowledge of the reliability of ice-templated ceramic-polymer composites, underlying deformation mechanisms, and predicting their compressive strength.

1.7 Proposed research

The purpose of this dissertation is many-folds with a central theme of tunable compressive response by addressing the microstructure-mechanical property relationships in both ice-templated ceramics and infiltrated ceramic-polymer composites. The findings of this dissertation would help establish guidelines to design ice-templated materials with tunable mechanical properties for
targeted structural and impact energy absorption applications. In this work, Chapter 2 and Chapter 3 discuss the novel methodology developed to employ AC electric fields in ice-templating. For the rest of the dissertation, Chapters (4-8) ice-templated ceramics were fabricated without applying the AC electric field.

Establishing a novel AC electric field-assisted ice-templating process requires exploring the interactions between the applied field and suspended ceramic particles in the aqueous medium. The influence of AC electric field parameters such as frequency, voltage, and field duration must be explored at different solids loading. It is to note that there are two methods to explore the AC electric-field assisted ice-templating process. First, the AC electric field can manipulate the particles in the aqueous suspensions and then implement the ice-templating process. Second, being a simultaneous AC electric field application during the ice-templating process. This dissertation explores the first method, applying a field to manipulate the spatial distribution of suspended particles and then exploring the effects on the ice-templating process.

The initial experiments revealed a frequency dependent on mass accumulation on metal electrodes. The magnitude and direction of mass accumulation were controllable. Applying the AC electric field across aqueous alumina suspensions resulted in the generation of the DC electric field, which varied with field duration, solid loading, and dispersant concentration. In Chapter 2, a thorough investigation was performed on understanding the role of individual constituents of aqueous alumina suspensions on the generated DC electric field. The mass accumulated on the metal electrode inherently resulted in a local change in suspension concentration. At the same time, a reminder of the suspension was in well-dispersed form. Empirical relations were derived to estimate the amount of mass accumulation as a function of electrical conductivity and concentration of dispersant in aqueous ceramic suspensions.
The objective of Chapter 3 is to understand the effects of local concentration change in the ice-templating process of aqueous ceramic suspensions. In this study, the accumulated mass on the metal electrode was varied by changing the AC electric field duration, followed by a unidirectional ice-templating process. This study explores the influence of local concentration on the microstructure evolution and uniaxial compressive mechanical response.

Chapter 4 investigates the uniaxial compressive response of ice-templated porous ceramics as a function of porosity, microstructure, and strain rate. This study explores the damage evolution and failure behavior at quasistatic and dynamic loading conditions. Further, this study aims at establishing a design guideline to fabricate ice-templated materials for desired mechanical performance. Chapter 5 explores the role of microstructure on the sphere impact response and damage morphology in ice-templated porous ceramics. The microstructure was systematically varied by changing the FFV. The influence on the direction of impact relative to growth direction was explored.

Chapter 6 presents the uniaxial compressive response of ice-templated ceramic-polymer composites in quasistatic and dynamic loading conditions. Furthermore, the compressive mechanical properties of porous, epoxy, and composites at different loading rates were investigated. Finally, an attempt was made to estimate the compressive strength based on the rule of mixtures and mode of failure.

Chapter 7 presents the role of loading direction on the uniaxial compressive response of ice-templated ceramic-polymer composites. This study explores the fundamental microstructure mechanical property correlations as a function of loading direction relative to layer orientation. This study investigates the role of layer connectivity and solid loading under quasistatic
compressive loads. Further, using the Tsai-Hill failure criterion, the role of competitive failure mechanisms on the compressive response of composites was evaluated.

In Chapter 8, the inelastic deformation mechanisms that evolve in ice-templated ceramic-polymer composites under compressive loading conditions that lead to macroscopic failure were explored. This study attempts to understand the underlying inelastic deformation mechanisms in ice-templated ceramic–polymer composites under compressive loading to investigate structure–mechanical property relationships and hierarchical materials design. Finally, Chapter 9 summarizes the work performed in this dissertation.
CHAPTER 2
CONTROLLED CHANGE OF LOCAL CONCENTRATION IN AQUEOUS CERAMIC SUSPENSIONS USING AC ELECTRIC FIELD AND IMPLEMENTATION TO THE FABRICATION OF ICE-TEMPLATED CERAMICS

2.1 Introduction

Colloidal processing is a useful route to synthesize ceramic bulk structures and films through careful control of initial suspension “structure” and its evolution during fabrication [73]. In colloidal processing, particle–particle interactions play an essential role in ceramic synthesis, and the methodologies that can manipulate these interactions and the state of aqueous ceramic suspensions are of profound fundamental interest to tailor final microstructure and properties. Energized fields such as the magnetic, mechanical, and electric fields allow to achieve extrinsic manipulation position and orientation of individual particles suspended in a media, potentially enabling assembly of particles [21]. Particles of any shape in nonhomogeneous field will experience both rotation and translation [74]. In recent years, manipulation of ceramic particles specifically in aqueous media using externally energized fields has gained significant attention for the fabrication of novel hierarchical ceramics and ceramic-based composites with the aim to achieve superior properties and property synergy.

Among the various colloidal fabrication techniques, freeze-casting, also known as ice-templating, has emerged as a novel method to fabricate bio-inspired ceramics and ceramic composites [21,49,50,75]. The porosity of ice-templated materials is a strong function of the solid
loading of aqueous suspensions [25,76]. Intrinsic parameters such as particle size and shape [25], freezing front velocity (FFV, growth velocity of ice crystals) [77–79], and water-soluble additives [80–82] that have been used to tailor microstructure and properties of ice-templated ceramics. On the other hand, in recent years, extrinsic manipulation of ice-templated ceramic microstructure has been attempted using magnetic field [21,32,33], ultrasound [21,83], and direct current (DC) electric field [36,40]. Among these external fields, the use of magnetic field in freeze-casting of ceramics has been relatively extensive. However, since ceramic materials are nonmagnetic or weakly magnetic, ferrimagnetic iron oxide (Fe₃O₄) nanoparticles were used to surface magnetize ceramic particles and make the ceramics respond to the external magnetic field [32]. Magnetic freeze-casting has been performed using permanent magnets, which, however, encounters with the problem of nonuniform field and thus microstructure nonuniformity [84]. Therefore, Helmholtz coils have been used to achieve uniform magnetic field [85]. Use of magnetic field has been shown to improve structural alignment in the direction transverse to the growth direction of ice crystals [84]. Magnetic freeze-casting has been shown to improve alignment of lamella walls, increase lamellar bridge density and bridge thickness, and enhance compressive mechanical properties in the direction transverse to the ice-growth direction [33,84]. Using acoustic pressure waves, Ogden et al. [83] fabricated ice-templated titania (TiO₂) materials with alternate concentric dense/porous rings. Tang et al. [36] applied a DC electric field perpendicular to the direction of the applied temperature gradient where electrodes also induced freezing. With the increasing field strength, lamella walls in ice-templated alumina (Al₂O₃) were increasingly aligned along the field direction, and compressive strength increased in that direction. Zhang et al. [40] prepared dense/porous bilayered ice-templated Al₂O₃ by applying DC electric fields during freeze casting. With the
increasing field strength, lamella walls were increasingly aligned away from the direction of the applied temperature gradient and spacing of lamella walls increased by more than 5 times.

The authors recently developed a novel methodology that uniquely employed alternating current (AC) electric field to fabricate ice-templated Al₂O₃ materials [86]. In the methodology, AC field was first applied to an aqueous Al₂O₃ suspension, and then ice-templating (i.e., unidirectional freezing of the suspension) was performed. AC field resulted in a net motion of Al₂O₃ particles in the suspension due to DC voltage generation. Suspension concentration increased near one of the electrodes, which was controlled through AC frequency and field duration. In sintered materials, the thickness of non-templated bottom region increased with field duration, whereas templated microstructure turned increasingly dendritic with field duration. The AC electric field-assisted materials exhibited remarkably enhanced compressive strength without any change in porosity.

The current study builds on the previous work by the authors and the objectives are manifolds, crucial to realize the potential of AC fields in the ice-templating of ceramics. The previous investigation revealed that the application of AC field to aqueous ceramic suspension resulted in DC voltage. Here, a series of studies were performed to determine the influence of electrical conductivity and ceramic loading of aqueous suspensions on DC voltage generation in the suspensions. Next, the influence of the generated DC voltage on the accumulation of ceramic particles on a metal electrode was studied for different solid loadings of ceramic suspensions. Finally, these findings were utilized in the ice-templating of ceramics to develop process–structure–mechanical property relationships and predictability for microstructure development.

2.2 Experimental
2.2.1 Materials and preparation of aqueous ceramic suspensions

Commercially available ultrafine alpha-alumina ($\alpha$-Al$_2$O$_3$, $d_{50} = 0.3$ µm, APA-0.5 Sasol, Tuscan, AZ) powder (referred to as UA) was used to prepare aqueous suspensions of 15, 20, 26, 30 and 35 vol% solid loadings, referred to as UA-15, UA-20, UA-26, UA-30, and UA-35, respectively. Each suspension was prepared in a Nalgene bottle using the following methodology. First, the required quantity of ceramic powder was mixed with deionized (DI) water containing anionic dispersant ammonium polymethacrylate (Darvan-C, R.T. Vanderbilt Co, Norwalk, CT). For each composition, four different wt% (0.5, 1, 1.5 and 2 wt%, with respect to Al$_2$O$_3$ powder) of Darvan-C ($C_w$) were used to prepare the suspensions. Each suspension was milled for 24 hours using zirconia (ZrO$_2$, 5 mm diameter) spheres. At the end of the mixing cycle, the suspension was sieved to separate the milling media and de-aired in a vacuum (pressure 0.1 MPa) for 30 minutes.

2.2.2 Measurements of viscosity, conductivity, and DC voltage

Viscosity of all the aqueous Al$_2$O$_3$ suspensions were measured using Anton Paar MCR302 rheometer at room temperature. During the measurement, shear rate was varied from 0.1 to 5 s$^{-1}$. For each composition, three measurements were conducted to check for reproducibility. Electrical conductivity ($K$) of DI water solutions (DI water-dispersant) and ceramic suspensions (DI water-Al$_2$O$_3$-dispersant) was measured using a benchtop meter HI5522 (HANNA Instruments, Smithfield, RI), which can measure $K$ up to 1000 mS/cm. All the measurements were performed at room temperature. The previous study by the authors revealed that DC voltage was generated upon application of AC voltage to aqueous Al$_2$O$_3$ suspensions containing DI water, ceramic powder, and Darvan-C [86]. In this work, AC voltage was first applied to solutions of DI water and Darvan-C and DC voltage, if any, was measured. Next, DC voltage measurements were performed for Al$_2$O$_3$ suspensions of different solid loadings and Darvan-C concentrations.
Measurements were also performed for suspensions only containing Al₂O₃ powder and DI water; however, those measurements were limited to low ceramic loading suspensions (18 vol%) since higher solid loading suspensions could not be prepared without dispersant.

2.2.3 Experimental setup for AC voltage application and DC voltage measurement

Figure 9a shows a schematic of the experimental setup used to apply AC electric field to DI water solutions and aqueous ceramic suspensions through two co-axial parallel metal electrodes of the same dimensions with 18 mm gap between electrodes, and measure DC voltage. The mold used was a hollow Teflon tube of 18.5 mm inner diameter, and the electrode material was 1018 low carbon steel. Electrode surfaces were prepared by grinding with 120, 320, and 600 grit silicon carbide (SiC) papers and finally polishing with 1200 grit SiC paper.

The mold was filled with solution/suspension by pouring from the top. The top electrode was then inserted into the mold, and it was ensured that both electrodes were in complete contact with the solution/suspension in the mold. Electrodes were held firmly against the Teflon tube by a clamp. AC electric field was applied through a function generator (Tektronix AFG 3102) and voltage amplifier (Tegam model 2340), whereas AC voltage across the electrodes during the experiment was monitored through an oscilloscope (Tektronix TDS 1002). A digital multimeter, DMM, (Fluke 8010A) was employed to detect any DC voltage between the electrodes. AC field experiments were performed at 250 kHz with applied peak-to-peak voltage (V<sub>pp</sub>) 190 V. In each experiment, field was applied for 10 minutes.

In a recent study [86], the authors revealed that when an AC field was applied to an aqueous ceramic suspension, the suspension became concentrated near one of the electrodes only and was also stuck to that electrode in the form of viscous paste, Figure 9b. Although the polarity of an AC field changes continuously, the results suggested a net motion of ceramic particles in aqueous
media. Since the number of particles that accumulate on an electrode could be affected by the direction of particle motion relative to the gravity, electrode configuration was used such that particles migrated upward and accumulated on the top electrode. For this purpose, top and bottom electrodes were reference electrode (R) and source electrode (S), respectively, Figure 9c. Here, the electrode attached to the terminal supplying the AC signal is referred to as the S electrode, whereas the other electrode is referred to as the R electrode. During each experiment, temperature change in the R electrode with time was measured through the thermocouple (T type) attached to the electrode. Temperature change in the electrode was considered as a measure of the temperature change in solution/suspension.

![Figure 1](image)

**Figure 1:** (a) Schematic representation of experimental setup for AC field application to aqueous ceramic suspension. (b) Optical image of the electrode with concentrated suspension near one of the electrodes in the form of viscous paste. (c) Schematic representation denoting the accumulation of particles on electrode S after application of AC field for 10 min at 1 kHz, 190 V.

A series of experiments were performed to study the influence of ceramic suspension composition and Darvan-C concentration on the accumulation of ceramic particles on the top
electrode. After each experiment, the top was carefully removed from the mold and placed in an oven for 1 h at 140 °C for complete drying. The difference between the mass of the electrode with ceramic particles and the mass of the electrode before the experiment provided the mass of ceramic particles accumulated on the electrode surface.

2.3 Results

2.3.1 Conductivity and DC voltage generation in DI water-dispersant solutions

The measurements were performed for DI water-dispersant solutions of different Darvan-C concentrations up to 1.6 (w/v)% . Here, dispersant concentration (C<sub>w/v</sub>) is expressed as weight of Darvan-C with respect to DI water volume in suspension. AC voltage remained constant when applied to DI water (ionic conductivity 1.4 μS/cm) and no DC voltage was detected. For DI water solutions with C<sub>w/v</sub> up to 0.4 (w/v)%, the change in the magnitude of the applied AC voltage during the experiments was negligible and DC voltage of very small magnitude (< 0.5 V) was detected and hence corresponding plots are not shown here. However, for C<sub>w/v</sub> above 0.4 (w/v)%, the magnitude of detected DC voltage was significant, which increased with dispersant concentration.

Figure 10a-c shows variations of measured AC voltage and DC voltage with field duration (t) for DI water solutions with C<sub>w/v</sub> of 0.54, 0.76 and 1.57 (w/v)%. In each figure, conductivity (K) of DI water solution is mentioned. At C<sub>w/v</sub> 0.54 (w/v)%, up to 2 minutes, DC voltage was negligible but increased to about 5 V by 4 minutes, whereas AC voltage decreased. Similar features are observed at higher concentrations as well; however, with increasing C<sub>w/v</sub>, the time taken for DC voltage generation gradually decreased. The trend in decrease of the time taken for DC voltage generation with C<sub>w/v</sub> is shown in Figure 10d.
Figure 2: (a-c) Variations of measured AC voltage and DC voltage with field duration ($t$) for DI water solutions. (d) Variation in the time taken for DC voltage generation for DI water solutions. (e) Variation of maximum DC voltage measured and $K$ of DI water solutions. (f) Variation of maximum DC voltage measured with $K$ of DI water solutions.

Therefore, at low dispersant concentrations, with the AC field applied, it took much longer time before DC voltage was generated but duration decreased markedly with $C_{w/v}$. Figure 10e shows variation of maximum DC voltage measured and $K$ of DI water solutions with $C_{w/v}$. $K$ of DI
water solutions increased linearly with $C_{w/v}$ reaching 2000 $\mu$S/cm at 1.6 (w/v)$\%$, whereas maximum DC voltage increased linearly above 0.4 (w/v)$\%$.

Therefore, current results revealed two important features on DC voltage generation in DI water solutions containing dispersant molecules with AC electric field applied. One is a threshold conductivity for generation of DC voltage. Second is that above threshold $K$, the magnitude of DC voltage increased linearly with $C_{w/v}$. Thus, current results revealed a strong correlation between $K$ of DI water solution and DC voltage, which is shown in Figure 10f.

2.3.2 Conductivity and DC voltage in aqueous alumina suspensions and accumulation of alumina particles on a metal electrode

Figure 11a shows variation of $K$ with ceramic content of suspensions prepared without Darvan-C. As a result, these measurements could have been performed up to 18 vol% ceramic loading only. $K$ increased with ceramic content and 18 vol% suspension exhibited $K$ of about 37 $\mu$S/cm, which is, however, well below than that of DI water solutions. Therefore, to prepare aqueous Al$_2$O$_3$ suspensions from low to high solid loading range (15 – 35 vol%) and increase $K$, all ceramic suspensions were prepared with different Darvan-C concentrations.

Figure 11b shows the variation of $C_{w/v}$ with ceramic content of suspension. On each plot, the number represents $C_w$ of suspensions. $C_w$ was converted to $C_{w/v}$ using the following equation:

$$C_w (%) = \frac{C_v(\%) \times \rho_s \times C_w}{100 - C_v(\%)}.$$  \hspace{1cm} (1)

$C_v$ is ceramic content (vol%) of suspension and $\rho_s$ ceramic density. Calculations were performed for a series of suspensions of different $C_v$ and $C_w$ with corresponding $C_{w/v}$ shown on y-axis. Thus, the amount of dispersant ($C_w$) required to achieve a targeted $C_{w/v}$ in ceramic suspension of any $C_v$
can be estimated. In Figure 11b, the shaded region corresponds to the composition range of ceramic suspensions (15 – 35 vol%) used in this work for fabrication of ice-templated ceramics.

Figure 3: (a) Variation of $K$ with ceramic content of suspensions prepared without Darvan-C. (b) The shaded region corresponds to the composition range of ceramic suspensions (15 – 35 vol%) used in this work for fabrication of ice-templated ceramics.
Figure 12 shows the results of $K$ (4a) and DC voltage (4b) measurements for UA-15, UA-20, UA-26, UA-30, and UA-35 suspensions prepared with different $C_{w/v}$. The general trend is that both increased almost linearly with $C_{w/v}$. Figure 12c shows variation of average % mass accumulation ($%m_c$) of $\text{Al}_2\text{O}_3$ particles on the top electrode surface with maximum DC voltage, where $%m_c$ increased with DC voltage. $%m_c$ was calculated by dividing $m_c$ (mass accumulated on electrode) with ceramic mass in suspension in the mold (Figure 9c). Therefore, Figure 12a-c revealed a strong correlation between $C_{w/v}$, $K$, maximum DC voltage, and $%m_c$. With increasing $C_{w/v}$, $K$ of aqueous $\text{Al}_2\text{O}_3$ suspensions increased, which enhanced maximum DC voltage that generated upon the application of AC field to ceramic suspensions, and, in turn, $%m_c$ increased. Figure 12d and 12e correlates maximum DC voltage and $%m_c$ with $C_{w/v}$, respectively. Finally, Figure 12f shows the dependence of $%m_c$ on $K$ of suspensions.
From the results presented in Figure 12, great insights of AC field-induced accumulation of ceramic particles on a metal electrode are obtained, and important conclusions can be made. The results revealed that $K$ of an aqueous ceramic suspension is a key factor in controlling $\% m_e$. By performing a linear fitting of the data in Figure 12f, an empirical equation is obtained as:

$y = 0.56x + 0.035$

$R^2 = 0.98$

$y = 26.5x$

$R^2 = 0.96$
\[ \%m_e = 26.5K. \] \hspace{1cm} (2)

From equation (2), for a targeted \( \%m_e \), the required \( K \) of aqueous Al\(_2\)O\(_3\) suspension can be approximately determined. As the results suggest, \( K \) of a suspension is governed by dispersant concentration. Therefore, by fitting the data in Figure 12a, another empirical equation is obtained as:

\[ K = 0.56C_{w/v} + 0.035. \] \hspace{1cm} (3)

Using equation (3), for the required \( K \) to achieve the targeted \( \%m_e \), the corresponding necessary \( C_{w/v} \) can be estimated. Recall that Figure 11b shows that same \( C_{w/v} \) can be achieved in Al\(_2\)O\(_3\) suspensions of different solid loadings (vol\%) depending on \( C_w \). Therefore, using the above equations (1-3), it is possible to estimate the amount of dispersant required for an Al\(_2\)O\(_3\) suspension to achieve a targeted \( \%m_e \), where dispersant controls conductivity of suspension which in turn controls accumulation of ceramic particles on a metal electrode. It is to be noted that there are other factors such as particle size, ceramic type, and material density that will affect the final outcome. Therefore, equations (2) and (3) may not be generalized based on the experiments performed here. Nevertheless, these equations should serve well for aqueous Al\(_2\)O\(_3\) suspensions prepared from sub micrometer size particles. Additionally, these equations will provide a guidance when performing similar experiments for other ceramic materials. As will be discussed in later sections, the above results are significant in employing AC electric field to tailor microstructure and strength of ice-templated ceramics without compromising with porosity.

### 2.3.3 Local change in suspension concentration due to AC field

The observations from AC electric field experiments suggested that not only particles accumulated on a metal electrode but also suspension became concentrated near the electrode. Therefore, it is anticipated that suspension concentration likely changed in the vicinity of the
electrode relative to bulk suspension concentration. Local change in ceramic suspension concentration is expected to influence number of ice crystals that generate and their growth characteristics during ice-templating process, and in turn templated microstructure. Therefore, it is important to determine local suspension concentration and its effect on the ice-templating process.

2.4 Conclusions

Application of AC electric field to aqueous ceramic suspensions resulted in the generation of DC voltage across the metal electrodes. This work revealed the influence of electrical conductivity and solid loading of aqueous ceramic suspensions on DC voltage generation. At the same time, the generated DC voltage led to the accumulation of particles on the metal electrode in aqueous ceramic suspensions. First, a systematic study demonstrated the influence of dispersant concentration on the electrical conductivity of aqueous solutions. This study revealed a critical dispersant concentration in an aqueous medium that dictates the generated DC voltage.

In contrast, the solid loading alone had minimal effect on the electrical conductivity of aqueous suspensions. Next, the influence of the generated DC voltage on the accumulation of ceramic particles on a metal electrode was studied for different solid loadings of ceramic suspensions for different amounts of dispersant. Finally, these findings were utilized to obtain empirical relations to estimate the amount of dispersant required for a ceramic suspension to achieve a targeted accumulated mass, where dispersant controls conductivity, which controls the accumulation of ceramic particles on a metal electrode. The results of this study, to modify local concentration by the accumulation of particles, were employed to fabricate ice-templated materials, as discussed in Chapter 3.
CHAPTER 3

AC ELECTRIC FIELD-ASSISTED FABRICATION OF ICE-TEMPLATED ALUMINA MATERIALS AND REMARKABLE ENHANCEMENT OF COMpressive strength

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3.1 Introduction

Strong interests have emerged in employing externally energized fields in the fabrication of novel ice-templated ceramics which exhibit aligned pore channels [34,35,40,87–89]. Porter et al. [87] applied a static magnetic field (0.12 T) perpendicular to the growth direction of ice crystals, which resulted in the preferred alignment of lamella walls on the plane perpendicular to growth direction in the resultant titania (TiO$_2$) materials, and the fabricated materials exhibited a two-fold increase in compressive strength in the transverse direction (perpendicular to growth direction) in comparison to the materials fabricated without field. Ogden et al. [34] used acoustic pressure waves to fabricate ice-templated TiO$_2$, resulted in structures with alternate concentric dense/porous rings. Tang et al. [88] applied a direct current (DC) electric field perpendicular to the direction of the applied temperature gradient with electrodes also induced freezing. With the increasing field strength, lamella walls in ice-templated alumina (Al$_2$O$_3$) were increasingly aligned along the field direction, and compressive strength increased in that direction. Zhang et al. [40] prepared
dense/porous bi-layered ice-templated Al₂O₃ by applying DC electric fields during freeze casting. This study reports a novel approach to fabricate ice-templated ceramics using alternating current (AC) electric fields, applied through two co-axial parallel metal electrodes to ceramic suspensions before the templating step. AC field increased the concentration of aqueous Al₂O₃ suspension near one of the electrodes and caused accumulation of particles on the electrode. It is revealed that AC fields can uniquely tune microstructure and markedly enhance compressive strength (without changing porosity) of ice-templated ceramics by exploiting the local increase in suspension concentration, demonstrating the great potential of AC fields in ice-templated materials development.

3.2 Experimental

3.2.1 Materials and preparation of aqueous ceramic suspensions

26 vol% aqueous Al₂O₃ suspensions were prepared from the Ceralox APA-0.5 powder (d₅₀ = 0.3 μm, Sasol, Tuscan, AZ). Aqueous suspensions were of 26 vol% solid loading. Ceramic suspension was prepared in a Nalgene bottle using the following methodology. First, the required quantity of ceramic powder was mixed with deionized (DI) water containing 1 wt% (of ceramic powder) anionic dispersant ammonium polymethacrylate (Darvan-C, R.T. Vanderbilt Co, Norwalk, CT). Next, the suspension was milled for 24 hours using zirconia (ZrO2, 5 mm diameter) spheres. At the end of the mixing cycle, the suspension was sieved to separate the milling media and then de-aired in a vacuum (pressure 0.1 MPa) for 30 minutes. A few drops of aqueous suspension were taken on a carbon tape and dried in an oven at 120 °C for 2 hours. Figure 13a shows scanning electron microscope (SEM, Phenom Pure) image of the dried powder sample, confirming ultrafine particle size (< 1 μm).
**Figure 5:** (a) SEM micrograph of as received Al₂O₃ powder. (b) Schematic representation of experimental setup for AC field application to aqueous ceramic suspension. (c) Representative optical micrograph of the polished steel electrode.

### 3.2.2 Experimental setup and conditions

Figure 13b shows a schematic of the experimental setup for AC field application to aqueous ceramic suspension. The electrode attached to the terminal supplying the AC signal is referred to as the source electrode (S), whereas the other electrode is referred to as the reference electrode (R). Temperature change in the R electrode with time was measured through a thermocouple. Initial experiments interestingly revealed that due to field, suspension became concentrated near one of the electrodes only and was also stuck to that electrode in the form of viscous paste (Figure 14). While the polarity of the AC field changes continuously, the preliminary results suggested a net motion of ceramic particles in aqueous media. A series of experiments were performed to study the influence of the AC field parameters on the accumulation of ceramic particles on one of the electrodes. Between 0.1 – 1000 kHz, ceramic suspensions were subjected to peak-to-peak voltage (Vₚₚ) of 190 V. At 1.5 and 2 MHz, applied Vₚₚ was 130 and 100 V, respectively. Another
interesting finding was that particles accumulated on the S electrode below 50 kHz and above 1000 kHz. Whereas between 50 and 1000 kHz, particles accumulated on the R electrode (Figure 14a and 14b).

![Image of electrode with particles](image)

**Figure 6:** Optical image of the electrode with concentrated suspension near one of the electrodes in the form of viscous paste.

Thus, the direction of particle migration was frequency-dependent. Since the number of particles that accumulate on an electrode could be affected by the direction of particle motion relative to the gravity, electrode configuration was used such that particles migrated upward and accumulated on the top electrode. To enable this, below 50 kHz and above 1000 kHz, top and bottom electrodes were S and R, respectively (Configuration-A, Figure 15c). Between 50 and 1000 kHz, top and bottom electrodes were R and S, respectively (Configuration-B, Figure 15d). After the completion of each experiment, the electrode on which ceramic particles accumulated was carefully removed from the mold and placed in an oven for 1 h at 140 °C for complete drying. The difference between the mass of the electrode with ceramic particles and the mass of the electrode before the experiment provided the mass of ceramic particles accumulated on the electrode surface.
Figure 7: (a) Optical images and schematic representation denoting the accumulation of particles on electrode S after application of AC field for 10 min at 1 kHz, 190 V. (b) Optical images and schematic representation denoting the accumulation of particles on electrode R after application of AC field for 10 min at 1000 kHz, 190 V. (c) Schematic representation of electrodes in Configuration-A. (d) Schematic representation electrodes in Configuration-B.
3.2.3 Fabrication of ice-templated ceramics

Next, field-induced accumulation of particles on an electrode was used in the fabrication of ice-templated Al₂O₃. The objective was to exploit the local change in suspension concentration to manipulate the growth characteristics of ice crystals and resultant ice-templated microstructure. In the fabrication experiments, electrode configuration was such that particles migrated downward and accumulated on the bottom electrode. The field was first applied to suspension, followed by ice-templating; Figure 16a. A custom-made device was used for ice-templating [19]. Templated samples were freeze-dried and sintered at 1550 °C for 4 hours. Few sintered samples were sectioned into thin disks (~1 mm) to evaluate porosity variation along the sample height, Figure 15b. The microstructure was analyzed using a scanning electron microscope (SEM). A 3 mm thick disk at the height of 5 mm from the bottom of several sintered samples was extracted for compression tests, Figure 16b.

3.2.4 Characterization of porosity, microstructure, and uniaxial compressive response

Ice-templated sintered Al₂O₃ samples were obtained in the form of cylinders. The density of sintered sample (ρ*) was determined from the measurements of mass and dimensions, whereas relative density (ρr) was calculated as ρr = ρ*/ρs, taking bulk density ρs of Al₂O₃ as 3.96 g/cm³. Total porosity was estimated as pᵣ = (1 − ρr) × 100. In addition, few samples were sectioned into thin disks (about 1 mm thickness), which were used to evaluate porosity variation along the height of the samples (Figure 16b). This step was performed for sintered materials fabricated with and without an AC field. Microstructure in the sintered materials was investigated using a desktop scanning electron microscope (SEM, Phenom Pure, Thermo Fisher Scientific). Both horizontal and vertical cross-sections of the samples were investigated under SEM for microstructure analysis (Figure 16b). From several sintered samples, 3 mm thick disk at the height of 5 mm from the
bottom of the samples was extracted for the uniaxial compression test (Figure 16b). Samples were compressed at a displacement rate of 0.5 mm/min (resulting in a strain rate of $10^{-3}/s$) using a mechanical testing machine (MTS, ALLIANCE RF/300). In this setup, the upper compression platen is attached to a spherical seat for improved alignment and ensuring even pressure across the entire surface of the specimen. During each experiment, surfaces of the compression platens in contact with the specimen surfaces were lubricated.

![Diagram](image)

**Figure 8:** (a) Schematic representation of the fabrication methodology denoting application of AC field to ceramic suspensions such that particles migrated towards bottom electrode and followed by ice-templating process. (b) Schematic representation denoting the microstructural and mechanical characterization performed on the sintered materials.
3.3 Results and discussion

Figure 17a and 17b show the variation in the average % mass accumulation ($m_e$) of Al$_2$O$_3$ particles on the electrode surface and temperature rise ($\Delta T$) in the electrode, respectively, with frequency. $m_e$ was estimated by dividing $m_e$ (mass accumulated on electrode) with ceramic mass in suspension in the mold. $m_e$ was strongly frequency-dependent and reached a maximum (over 30%) between 250 – 500 kHz. $\Delta T$ also exhibited similar frequency dependence. Temperature increase in the electrode was considered as the temperature rise in suspension.

Figure 17c shows an almost linear increase in $m_e$ with field duration ($t$) at 1, 100, and 250 kHz. The increase in $m_e$ also suggests an increase in suspension concentration near the electrode. A digital multimeter (DMM) was employed to detect, if any, DC voltage between the electrodes. Figure 17d shows the variation of AC voltage and DC voltage with $t$ at 250 kHz measured using oscilloscope and DMM, respectively. With turning field ON, AC voltage immediately dropped whereas DC voltage increased to a maximum at the same $t$. With the increasing $t$, AC voltage and DC voltage gradually increased and decreased, respectively. It appears that DC voltage was generated at the expense of AC field energy.

Measurements revealed that DC voltage was maximum at the frequencies where $m_e$ was also maximum, suggesting a direct correlation between DC voltage generation and ceramic particle accumulation on the electrode. Due to the induced DC voltage, negatively charged Al$_2$O$_3$ particles (due to Darvan C dispersant) traveled towards the positively charged electrode and accumulated on the electrode. Thus, a net motion of ceramic particles occurred in aqueous media, similar to the electrophoretic motion in the DC field, despite the external AC electric field.

The exact origin of DC voltage generation due to the applied AC field and frequency dependence is not currently understood and will be explored in a future study. However, Chang et
al. [90] showed that in miniature semiconductor diodes suspended in aqueous media subject to AC field, DC voltage across the diode electrodes generated due to the rectification effect induced by the AC field. It is possible that metal electrodes in combination with aqueous ceramic suspension also exhibited the behavior of a typical diode due to the AC field rectification effect, as schematically depicted in Figure 17e. The important takeaway is that the magnitude and direction of DC voltage are frequency-dependent, and thus the direction and accumulation of ceramic particles can be manipulated by varying AC frequency.

Based on the above results, in the fabrication experiments, the AC field was applied at 250 kHz where ceramic accumulation was maximum, and particles migrated toward the bottom electrode, which also acted as the “Cold-finger” where ice crystals nucleated during freezing. While all the fabrication experiments were performed at 250 kHz, field duration was systematically changed to control local changes in suspension concentration. Figure 18a shows the variation of ceramic vol% ($C_s = \rho_r \times 100$) in sintered $\text{Al}_2\text{O}_3$ with $t$. $\rho_r$ is relative density. Samples fabricated with field exhibited only a slight increase in $C_s$, with a noticeable difference at longer $t$. With the increasing $t$, sample height decreased slightly, but sample diameter was unchanged (not shown). Figure 18b shows the variation in $C_s$ along the sample height (i.e., growth direction) for different $t$, estimated from 1 mm thin disks. Expectedly, $C_s$ is almost constant along the height in control samples. With the field application and increasing $t$, $C_s$ in the bottommost disk increased markedly; also see Figure 18c. $C_s$ in the bottommost disk without the field is ~40 vol% but increased even at 2 minutes. At 3 minutes, $C_s$ increased to 60 vol% and reached over 80 vol% at 10 minutes. The increase of $C_s$ in the bottommost disk is directly related to the enhanced concentration of particles with $t$ in the suspension in the vicinity of the bottom electrode, whereas concentration change was negligible in the rest of the suspension. Local ceramic concentration ($C_l$)
in the bottommost region of the suspension in the mold was approximately estimated. Since the bottommost disk (diameter 15 mm and thickness 1 mm) exhibited the maximum $C_s$, $C_l$ was estimated within this volume.

**Figure 9**: Variation in the (a) average % mass accumulation ($\% m_e$) of Al$_2$O$_3$ particles on the electrode surface and (b) temperature rise ($\Delta T$) in the electrode with frequency. (c) Variation of $\% m_e$ with field duration ($t$) at 1, 100, and 250 kHz. (d) Variation of AC voltage and DC voltage with
$t$ at 250 kHz. (e) Schematic representation of AC field application to ceramic suspension and the rectified DC field causing ceramic particle motion.

From the sintered ice-templated Al$_2$O$_3$ materials, 1 mm thin disks were extracted to estimate the ceramic content along the specimen height i.e., ice-growth direction. For each disc extracted along the specimen height, the sintered density ($\rho^*$) was determined from the measurements of mass ($m_d$) and volume ($v_d$). Note, the volume ($v_d$) was calculated from the dimensions of each extracted disc. The relative density ($\rho_r$) was calculated as $\rho_r = \rho^*/\rho_s$, where $\rho_s$ is the bulk density of dense $\alpha$-Al$_2$O$_3$ (3.96 g/cm$^3$).

**Figure 10:** (a) Variation of ceramic vol% ($C_s = \rho_r \times 100$) in sintered Al$_2$O$_3$ with $t$. (b) Variation in $C_s$ along the sample height (i.e., growth direction) for different $t$, estimated from 1 mm thin disks. (c) Variation of $C_s$ in the bottommost disk of sintered Al$_2$O$_3$ and variation of local ceramic concentration ($C_l$) in bottommost region of suspension of mold for different $t$. 

An approximate estimation of local ceramic concentration ($C_l$, vol%) in the bottommost region of the suspension in the mold was performed by the following steps. First, by measuring the average shrinkage ($\nu_s$, vol%) of green specimens (as ice-templated frozen specimen) with respect to sintered samples. The green specimens on an average showed a decrease of 41.5 vol% after the sintering step. Note, here the green specimen was assumed to shrink uniformly. Secondly, the approximate volume of section ($\nu_i$) prior to sintering i.e., volume equivalent to the bottommost disc was calculated as, $\nu_i = \frac{\nu_d}{(1-\nu_s)_{100}}$. Thus, the estimated volume of section ($\nu_i$) occupied by bottommost section in the green specimen was obtained. Further, the volume of ceramic particles ($\nu_c$) was calculated as $\nu_c = \frac{md}{\rho_s}$. Finally, the estimated solid loading ($C_l$, vol%) was calculated as, $C_l = \frac{\nu_c}{\nu_i} \times 100$. Figure 18c shows that up to 2 minutes, change in $C_l$ was relatively negligible. At 3 minutes, $C_l$ increased to about 36 vol% and to 48 vol% at 10 minutes. Therefore, these calculations revealed how much $C_l$ increased due to the AC field relative to bulk suspension concentration (26 vol%).

Figure 19a-d shows SEM images of vertical cross-section (up to 1900 $\mu$m from bottom) of sintered samples fabricated without and with the field. The microstructural observations made from each sintered sample are representative for the corresponding fabrication conditions. At the beginning of freezing, ice crystals grow rapidly and engulf particles [91–93]. As a result, a dense, thin non-templated region develops at the bottom of sintered materials, which can be seen in the material fabricated without field (Figure 19a). However, the thickness of the non-templated layer increased with $t$, with a marked increase at 10 minutes, attributed to field-induced increased concentration of particles in the bottom region.
Higher magnification SEM images of bottom regions (Figure 19e-h) revealed that grain size increased with $t$, supporting increased particle concentration and particle packing in green samples, facilitating mass transfer during sintering and grain growth. Figure 19i-l shows SEM images of a plane perpendicular to the growth direction and at the height of 1200 $\mu$m from the bottom. Without field and at 3 minutes, completely templated microstructure developed by this height. However, at the same height, the microstructure was partially templated at 5 minutes but non-templated at 10 minutes. Thus, Figure 19 revealed a strong influence of AC field on microstructure development at the beginning phases of ice-templating, suggesting that the increased concentration of Al$_2$O$_3$ particles near the bottom electrode delayed the transition from non-templated to templated microstructure. In Figure 19a-c, lamella walls are aligned along the growth direction in the templated region. At 10 minutes (Figure 19d), lamella walls are almost perpendicular to the growth direction.

Figure 20a-d show SEM images of a plane perpendicular to the growth direction and at the height of 5 mm from the bottom of sintered samples. Higher magnification SEM images in Figure 20e-h provide further insights into microstructure developments. The characteristic ice-templated microstructure is observed for all the fabrication conditions but turned increasingly finer with $t$. Without the field (Figure 20a), morphology is lamellar with lamella wall thickness ($\delta$) 8.5 $\pm$ 2.4 $\mu$m and lamellar bridge density ($\rho_b$) 272.6 $\pm$ 23.6 mm$^{-2}$. $\rho_b$ is defined as the number of bridges present in between the adjacent lamellae walls per unit area [24]. At 3 minutes (Figure 20b, f), $\delta$ decreased to 7.3 $\pm$ 2.5 $\mu$m, and $\rho_b$ increased significantly to 822.5 $\pm$ 113.4 mm$^{-2}$, resulting in dendritic morphology. At 5 minutes (Figure 20c, g), morphology appears more dendritic with $\delta = 7.3 \pm 3.1 \ \mu$m and $\rho_b = 836.3 \pm 80.3 \ \text{mm}^{-2}$. In addition to long pore channels between the lamella walls (the characteristic ice-templated microstructure), there are regions with the walls containing
small pores, as indicated by yellow dashed ellipses in Figure 20g. By 10 minutes (Figure 20d, h), the fraction of small pores within the walls increased markedly, as indicated by a yellow dashed ellipse in Figure 20h. Figure 20a-h suggests that the primary effect of the AC field was in enhancing connectivity between lamella walls and turning the morphology dendritic. However, prolonging AC field duration to 10 minutes had additional effects on microstructure, which may not be desirable.

Therefore, increased concentration of particles in suspension near the cold-finger where ice crystals first formed likely resulted in the development of finer ice crystals compared to that without the field. To shed light on this aspect, bottom regions of sintered samples fabricated without and with field (3 minutes) were further characterized using SEM. From the bottom of one representative sintered sample for each condition, materials were removed in small thickness (~200 μm) along the growth direction, and horizontal cross-sections were imaged.

Figure 20i-p shows SEM images at different heights for the material fabricated without (i-l) and with field applied for 3 minutes (m-p). Without the field, at the height of 200 μm, the microstructure contains randomly oriented (cellular) pores and characteristic ice-templated microstructure developed by 400 μm. With field, the dense region is seen even at 400 μm, cellular pores evolved by 600 μm, and the characteristic templated microstructure is evident at 800 μm. From Figure 20, it is evident that, first, increased local concentration of particles in suspension due to AC field delayed the evolution of templated microstructure. Second, the increased concentration of particles resulted in the development of finer microstructure, indicating that finer ice crystals formed during the templating step, which can be controlled.
**Figure 11:** (a-d) SEM images of vertical cross-section (up to 1900 µm from bottom) of sintered samples fabricated without (t = 0) and with field (3, 5, 10 minutes). (e-h) Higher magnification SEM images of bottom regions revealing increase in grain size with t. (i-l) SEM images of a plane perpendicular to the growth direction and at the height of 1200 µm from the bottom of sintered samples revealing microstructural development for different t.
Figure 12: (a-d) SEM images from plane perpendicular to growth direction revealing microstructure evolution at 5 mm height from bottom in sintered materials. Higher magnification SEM images provide further insights into microstructure: (e) lamellar morphology without field and (f-h) increasing dendritic morphology with field duration (3, 5, 10 minutes). At 5 minutes (g),
regions with walls containing small pores are observed, indicated by yellow dashed ellipses. By 10 minutes (h), the fraction of small pores within the walls increased markedly, indicated by a yellow dashed ellipse. SEM images at different heights along the growth direction for material fabricated without field (i-l) and field applied for 3 minutes (m-p).

Figure 21a-b schematically shows the role of the AC field in microstructure development. At the comparable freezing conditions, with the increasing suspension concentration, the microstructure of ice-templated materials also becomes increasingly finer [31,76,94]. Figure 21a shows ice crystals formed in a ceramic suspension of uniform concentration (without AC field). Figure 21b shows ice crystals developed in the same suspension where AC field applied before freezing resulted in a concentration gradient with concentration higher in the vicinity of the bottom electrode (Cold-finger), increasing the number of sites for ice crystal nucleation. As a result, more ice crystals formed in the concentrated region, which continued to grow upward even in the region of lower concentration. Therefore, the AC field-assisted process can result in a finer ice-templated ceramic microstructure than if the same suspension is solidified without applying field before the freezing step. Microstructure tuning will depend on the local concentration of ceramic particles (controlled by the AC field) at the freezing end, where ice crystals nucleate during the templating process.

Finally, Figure 21c-j shows the effects of AC field-assisted microstructure changes on the uniaxial compressive response (stress-strain curves), Figure 21c for control samples (no field), and Figure 21d-f for t of 3, 5 and 10 minutes. Average freezing front velocities (FFVs) for the materials are indicated. Porosity values of all the sintered disks tested in compression were comparable. Compared to control samples, field-assisted materials exhibited remarkably enhanced strength.
The trend is more clearly visible in Figure 21g, showing the variation of maximum compressive strength ($\sigma_m$) with $t$. For control samples, $\sigma_m$ is only $26.6 \pm 1.5$ MPa. With the increasing $t$, the average $\sigma_m$ almost linearly increased to $118.7 \pm 25.1$ MPa at 4 minutes. Between 3 and 5 minutes, materials exhibited remarkably higher $\sigma_m$ (3- to 4-fold) than control samples. Beyond 5 minutes, materials exhibited a decrease of $\sigma_m$; however, they still maintained significantly higher strength ($67.4 \pm 13.0$ MPa at 10 minutes) than control samples. Although the suspensions for different $t$ were ice-templated at the same gap between the Cold-finger and liquid N$_2$, FFV values decreased with $t$, mainly between 5 ($25.3 \pm 1.2$ $\mu$m/s) and 10 minutes ($21.1 \pm 1.0$ $\mu$m/s). With the decreasing FFV, the ice-templated ceramic microstructure becomes lamellar, and compressive strength decreases [24,94]. However, here, the strength decrease could be related to a gradual loss of characteristic ice-templated microstructure at higher field durations, as discussed before. Figure 21h and 21i show stress-strain curves at different FFVs for 0 and 3 minutes, respectively, whereas Figure 21j shows the variation of $\sigma_m$ with FFV for both conditions. Control samples showed only a moderate increase of $\sigma_m$ with FFV, whereas 3 minutes materials exhibited a marked increase with the strength gap increased with FFV.
**Figure 13:** (a-b) Schematic illustration of the role of AC electric field in ice-templated microstructural development. (a) Ice crystals formed in a ceramic suspension of uniform concentration. (b) Ice crystals developed in the same suspension where AC field before freezing resulted in a concentration gradient with concentration of particles higher in the vicinity of the cold-finger (bottom electrode). Greater number of ice crystals formed in the concentrated region, which continued to grow upward even in the region of lower concentration. Uniaxial compressive stress strain curves of materials fabricated (c) without and (d-f) with field (t of 3, 5 and 10 minutes).
(g) Variation of maximum compressive strength ($\sigma_m$) with $t$. Stress-strain curves at different FFV for materials fabricated (h) without and (i) with field ($t = 3$ minutes). (j) Variation of $\sigma_m$ with FFV for 0 and 3 minutes.

3.4 Conclusions

In the current work, the application of AC electric field to aqueous ceramic suspension generated DC field, resulting in a local increase of suspension concentration and accumulation of ceramic particles on a metal electrode, which can be controlled. The findings were used to develop a novel methodology, where an AC field was first applied to ceramic suspensions, followed by ice-templating. The results revealed that the changes in the local concentration of ceramic particles in the vicinity of the Cold-finger could be used for the controlled microstructure manipulation and remarkable improvement of compressive mechanical properties without changing porosity. The results also suggest that the local change of concentration up to 40 vol% relative to bulk suspension composition (26 vol%) was critical in achieving the maximum strength. Importantly ceramic particles responded to the AC field without the need for a second phase material. While beyond the scope of this work, the current results could not be achieved by directly applying DC electric field to ceramic suspensions, and the preliminary findings suggested a difference in the deposited ceramic layers between the fields. A dense layer also formed with a direct DC field application, similar to the work of Zhang et al. [40], but with no effect on templated microstructure and strength. Thus, the current work revealed the significant potential of AC electric fields to fabricate ice-templated materials. This work will significantly contribute to advancing ice-templated materials development using externally energized fields. The future studies will be extended to different ceramics and suspension concentrations, as well as AC field application during ice-
templating, to further understand the tunability of the methodology and process-structure-property relationships.

**Acknowledgments**

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CHAPTER 4
DIRECT OBSERVATION OF FAILURE IN ICE-TEMPLATED CERAMICS UNDER DYNAMIC AND QUASISTATIC COMPRESSIVE LOADING CONDITIONS

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4.1. Introduction

There is an increasing demand of mechanically robust lightweight materials for structural applications including scenarios where materials are subjected to high-strain rate (dynamic, \(\sim 10^3\) s\(^{-1}\)) loading conditions [95–99]. In natural porous solids hierarchical structure and oriented porosity attribute a synergy of mechanical properties as well as property anisotropy [4,100–102], and thereby provide important guidance to lightweight materials design. Ice-templating is an emerging technology that enables the development of ceramic materials with hierarchical structure and directional porosity [5,17,29,93,103]. In this technique, an aqueous ceramic suspension is unidirectionally solidified leading to the formation of alternating layers of ice crystal lamellae and ceramic particles, where the parallel layers are oriented along the growth direction of ice crystals. Ice crystal removal through sublimation process results in hierarchical ceramic materials with highly directional pores and walls, both oriented along the growth direction of ice crystals.
Sintering is performed to impart strength to macroporous ceramics while retaining the material morphology (lamellar/dendritic) that evolves during the unidirectional freezing step.

In our recent study [55], it was observed that uniaxial compressive stress-strain response of ice-templated ceramics in quasistatic strain rate regime (low-strain rate, $\sim 10^{-3}$ s$^{-1}$) strongly depended on porosity. With the decreasing porosity compressive response gradually transitioned from a damageable, cellular-like (progressive type) failure response to a brittle-like (catastrophic type) failure response. At high-strain rate ($\sim 10^3$ s$^{-1}$) compressive response was observed to be however damageable, cellular-like, irrespective of porosity. While our previous work provides useful information on the porosity and strain rate dependence of compressive mechanical properties in ice-templated sintered ceramics [55], the study focused on characterizing compressive response based on the property measurements and concentrated primarily on understanding the quasistatic compressive response. However, the macroscopic mechanical response of brittle solids is inherently related to the underlying processes of damage evolution leading to failure [104,105]. Toward this end, the goal of this study is to investigate the damage evolution mechanisms in ice-templated ceramics under dynamic and quasistatic uniaxial compressive loading conditions, in correlations to porosity and microstructure to provide greater insights into compressive mechanical properties.

To address the porosity dependence of damage evolution, we synthesized ice-templated alumina (Al$_2$O$_3$) materials from four different compositions of aqueous suspensions in the porosity range of 58–72 vol%. Whereas, to understand the microstructure dependence of damage evolution, for each composition we templated materials at different freezing front velocities (FFVs) to vary microstructure while maintaining porosity comparable across the resulting microstructures. Finally, to understand the dependence of damage evolution on the strain rate regime, we
characterized uniaxial compressive response at dynamic ($\sim 10^3 \text{ s}^{-1}$) and quasistatic ($\sim 10^3 \text{ s}^{-1}$) strain rates. Note that the duration of quasistatic compressive loading is on the order of minutes, whereas dynamic loading duration is 100–200 μs, a $10^6$ order difference of time-scale. We captured damage evolution and failure at macroscopic length-scale in ice-templated ceramics during compression tests employing a FASTCAM SA4 Photron camera, which can capture images in the speed range of few frames per second (suitable for low-strain rates) to over 100,000 frames per second (suitable for high-strain rates).

4.2 Experimental

4.2.1 Synthesis of ice-templated porous alumina materials

Ice-templated materials were processed from aqueous suspensions of ultrafine Al$_2$O$_3$ ($d_{50}=300$ nm, APA-0.5, Sasol, Tuscan, AZ) of four different compositions, 20, 22, 24, and 26 vol.%; the corresponding sintered porous Al$_2$O$_3$ materials will be referred to here as UA20, UA22, UA24, and UA26, respectively. For each composition, Al$_2$O$_3$ powder and an anionic dispersant (Darvan C, R.T. Vanderbilt Co., Norwalk, CT) were mixed first in deionized water in a Nalgene bottle, where Darvan C was taken in the proportion of 1 wt.% of Al$_2$O$_3$ powder. Next, zirconia (ZrO$_2$) spheres (~5 mm in diameter) were added to suspension and mixing of the suspension was conducted using a jar mill for 24 hours. After completion of the mixing cycle, an organic binder poly(2-ethyl-2-oxazoline) was added to the suspension (5 wt.% of Al$_2$O$_3$ powder) and the suspension was milled further for another hour. Afterward, the suspension was sieved to separate the ZrO$_2$ spheres and de-aired in low pressure for 30 min to remove any air bubbles entrapped in suspension. A custom-made device was employed for ice-templating of aqueous Al$_2$O$_3$ suspensions under unidirectional freezing condition [19]. This set up contains a thin steel plate
(“Cold-finger”) on which a Teflon tube is placed and filled with an aqueous ceramic suspension. Next, the entire assembly is inserted inside liquid nitrogen (N\textsubscript{2}) Dewar and placed above the liquid N\textsubscript{2} interface. As the temperature of the Cold-finger reaches below 0°C, ice crystals start to nucleate at the bottom of suspension and grow upward under the influence of applied temperature gradient. Freezing-front velocity (FFV) is controlled by adjusting the distance between the Cold-finger and liquid N\textsubscript{2} surface. In this study, for each composition, materials were produced in the form of a cylinder (~18.5 mm in diameter and ~20 mm in height). Templated samples were produced at different FFVs by adjusting the gap (1mm, 15 mm, 30 mm) between the Cold-finger and liquid N\textsubscript{2} surface. For each templated sample, average FFV was determined by dividing the height of a frozen sample with the time required for the completion of solidification \cite{19, 26}. Frozen samples were freeze-dried at low pressure (0.014 mbar) and temperature (-50°C) for 96 hours inside a freeze dryer (2.5L, Labconco, Kansas City, MI). Sintering was conducted in a box furnace (KSL-1700X, MTI Corporation, Richmond, CA) in an air atmosphere at 1550°C for 4 hours.

4.2.2 Characterization of ice-templated sintered porous Al\textsubscript{2}O\textsubscript{3} materials

From each sintered Al\textsubscript{2}O\textsubscript{3} cylinder sample two disks specimens were extracted (Figure 22a), which were utilized for the measurements of sintered density (\(\rho^*\)), relative density (\(\rho_r\)), and total porosity (\(\rho_t\)) as well as for characterization of compressive mechanical properties. Sintered density (\(\rho^*\)) was determined from measurements of mass and dimensions. Relative density (\(\rho_r\)) was estimated using \(\rho_r = \rho^*/\rho_b\), where \(\rho_b\) is the bulk density of \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (taken here as 3.96 g/cm\textsuperscript{3}). Total porosity was estimated as \(\rho_t = (1 - \rho_r) \times 100\). Figure 22b shows the representative cross-sectional plane (perpendicular to ice-growth direction) that was utilized for microstructure characterization, employing a desktop Phenom ProX scanning electron microscope (SEM).
4.2.3 Characterization of deformation and failure at low-strain and high-strain rates

Uniaxial compressive mechanical properties were characterized both at the low-strain rate ($\sim 10^{-3}$ s$^{-1}$) and the high-strain rate ($\sim 10^3$ s$^{-1}$) loading conditions; specimens were compressed parallel to the ice-growth direction. Figure 23 shows the experimental setups for both the loading conditions, Figure 23a for quasistatic loading and Figure 23b for dynamic loading. A FASTCAM SA4, Photron camera was employed to capture damage evolution and failure in the materials during compression tests. For quasistatic tests, an imaging speed of 60 frames per second was utilized with a resolution of 192×128 pixels, whereas for dynamic experiments an imaging speed of 100,000 frames per second with a resolution of 192×128 pixels was employed. Quasistatic experiments were performed using a mechanical testing machine (MTS, ALLIANCE RF/300) at a displacement rate of 0.5 mm/min (Figure 23a).

For high-strain rate experiments a split Hopkinson pressure bar (SHPB) set up was employed (Figure 23b). This set up consists of a solid striker bar of length 330.2 mm, a solid incident bar of length 1524 mm, and a solid transmission bar of length 914.4 mm; all the with a common diameter.
of 19.1 mm and are made of a high-strength aluminum (Al) alloy. Since longitudinal elastic stress wave propagation speed is significantly reduced in materials with high porosity (i.e., low impedance) compared to the counterpart bulk solid materials [106], Al alloy bar was utilized (instead of high strength maraging steel) to reduce impedance mismatch between the bar material and ice-templated sintered ceramic material, which facilitates transfer of elastic stress wave through specimen to transmission bar. In this setup, a striker bar impact on incident bar generates a compressive stress pulse that travels through the incident bar and loads specimen in uniaxial compression. During deformation, a part of the pulse transmits through the specimen to the transmission bar and the rest of the incident pulse is reflected back to the incident bar. Uniaxial compressive stress-strain response in the material is determined using the transmitted and reflected stress pulses.

![Figure 15: Schematics representing the experimental set up for characterization of deformation and failure at (a) low-strain rate (~10^{-3} \text{s}^{-1}), and (b) high-strain rate (~10^{3} \text{s}^{-1}) loading conditions.](image)

For testing of ceramic materials, it is important to achieve stress equilibrium in the elastic deformation regime prior to brittle fracture [107]. During the planar impact between metal striker bar and incident bar, elastic stress wave of trapezoid form develops that has a steep rise time of
loading stress. To achieve stress equilibrium in ceramic specimens before fracture, pulse shaping technique is commonly utilized to increase the rise time of the loading pulse [108]. In this work, for each SHPB experiment, a copper (Cu) pulse shaper was placed at the striker bar-incident bar interface to increase the rise time of the loading pulse. Figure 24a shows incident stress pulses without and with Cu pulse shaper. It can be seen that in the presence of Cu pulse shaper rise time was significantly enhanced compared to the loading pulse without the pulse shaper and high-frequency noises were removed. For testing of ceramic materials employing SHPB setup, a general requirement is that there should be 3-5 wave transits within a specimen to achieve force balance (i.e., equilibrium) before macroscopic failure in the material [107]. Longitudinal wave speed \( C_s \) in a solid is estimated as

\[
C_s = \sqrt{\frac{E_s}{\rho_s}},
\]

where \( E_s \) and \( \rho_s \) are Young’s modulus and density of the material, respectively [26]. As will be discussed later, porosity \( \rho^* \) in the ice-templated sintered Al\(_2\)O\(_3\) materials varied with both composition and FFV. Table 2 shows \( C_s \) of the sintered materials as a function of composition and freezing condition (i.e., the gap between Cold-finger and liquid N\(_2\)). \( E_s \) was determined from the slope of the initial regime of the elastic part of the quasistatic stress-strain curve. Transit time \( t_s \) for the leading edge of an incident wave to travel through a specimen is given by

\[
t_s = \frac{l_s}{C_s},
\]

where \( l_s \) is the length of the specimen. From Table 2, it can be seen that single transit time within the materials varied in between 2-7 \( \mu \)m, depending on the composition and freezing condition (Cold-finger gap). Figure 24a shows that the rising part of an incident pulse is about 60 \( \mu \)s, which
would ensure that there will be several wave reflections in the specimens before reaching peak stress.

**Table 2:** Variation of longitudinal wave speed \((C_s)\) and single transit time \((t_s)\) in ice-templated sintered porous \(\text{Al}_2\text{O}_3\) materials as a function of composition and freezing condition (Cold-finger gap)

<table>
<thead>
<tr>
<th>Composition ID (ceramic content in aqueous suspension)</th>
<th>Specimens extracted from sintered cylinder (\text{Al}_2\text{O}_3) samples</th>
<th>Gap (mm)</th>
<th>1</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA20 (20 vol%)</td>
<td>Wave speed, (C_s) (m/s)</td>
<td>749.7</td>
<td>671.5</td>
<td>410.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transit time, (t_s) (µs)</td>
<td>4.0</td>
<td>4.5</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>UA22 (22 vol%)</td>
<td>Wave speed, (C_s) (m/s)</td>
<td>786.3</td>
<td>755.8</td>
<td>425.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transit time, (t_s) (µs)</td>
<td>3.8</td>
<td>4.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>UA24 (24 vol%)</td>
<td>Wave speed, (C_s) (m/s)</td>
<td>1425.4</td>
<td>753.9</td>
<td>504.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transit time, (t_s) (µs)</td>
<td>2.1</td>
<td>4.0</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>UA26 (26 vol%)</td>
<td>Wave speed, (C_s) (m/s)</td>
<td>1508.7</td>
<td>1043.4</td>
<td>689.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transit time, (t_s) (µs)</td>
<td>2.0</td>
<td>2.9</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>

Stress pulses were measured through the strain gages (mounted in the middle of the incident and transmission bars) using a signal conditioning amplifier (2310B, Vishay) and a high-speed digitizer (NI PCI-5105, National Instrument). In this work, the universal general-purpose strain gages of linear pattern (CEA-13-250UW-350) type were utilized for the measurements of stress waves. Stress in a specimen is estimated as [109]

\[
\sigma(t) = E \varepsilon_T(t) \frac{A_t}{A_s}, \tag{3}
\]

where \(E\) is Young’s modulus of the bar material, \(\varepsilon_T(t)\) is the time-resolved axial strain in the transmission bar, and \(A_t\) and \(A_s\) are the cross-sectional areas of the transmission bar and sample, respectively. Similarly, strain rate in a specimen is calculated as [109]

\[
\dot{\varepsilon}(t) = -\frac{2C_o}{l_s} \varepsilon_R(t), \tag{4}
\]
where $C_0$ is the wave velocity of the bar material, $l_s$ is the original length of the specimen, $\varepsilon_R(t)$ is the time-resolved axial strain of the reflected pulse in the incident bar. Finally, strain in a specimen is calculated as [109]

\[
\varepsilon(t) = \int_0^t \dot{\varepsilon}_R(t).
\] (5)

Figure 24b shows the representative incident, reflected and transmitted signals measured from an ice-templated sintered porous Al$_2$O$_3$ specimen. Whereas, Figure 24b shows a comparison of the forces acting on the specimen from the incident end and transmitted end of the SHPB setup corresponding to the signals shown in Figure 24c, which suggests that stress equilibrium was achieved in the material prior to macroscopic failure.

**Figure 16**: (a) Modification of incident signal with the use of copper pulse shaper, (b) Representative strain gage signals obtained from the modified SHPB set-up of UA26 material, (c) Comparison of forces acting on the incident end and transmitted end of modified SHPB set-up for a UA26 material.
4.3 Results

4.3.1 Materials, porosity, and microstructure

Figure 25 shows the variation of total porosity ($\rho_t$) of the specimens extracted from the sintered Al$_2$O$_3$ cylinders with FFV for all the compositions. The average values of $\rho_t$ and FFV are listed in Table 3 for all the compositions. It can be seen from Table 3 that for each composition average FFV decreased consistently with the increasing gap. Figure 25 shows that there is a consistent decrease of porosity with the increasing solids loading (Al$_2$O$_3$ content) of suspension. For the UA20 materials, porosity is observed to be about 70.7 ± 1.1 vol.%, whereas the UA26 materials exhibited porosity about 59.5 ± 0.8 vol.%. For each composition, the increase of FFV resulted in a decrease of porosity, but the effect was more pronounced for the UA22 and UA24 materials. Overall, the porosity of materials is observed to be in the range of 58-72 vol.%.

Table 3: Variation of FFV and porosity ($p_t$) in ice-templated sintered Al$_2$O$_3$ materials with composition and “cold finger” gap.

<table>
<thead>
<tr>
<th>Composition ID</th>
<th>Specimens extracted from sintered cylinder Al$_2$O$_3$ samples</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition ID</td>
<td>Specimens extracted from sintered cylinder Al$_2$O$_3$ samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ceramic content in aqueous suspension)</td>
<td>Gap (mm)</td>
<td>1</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>UA20 (20 vol.%)</td>
<td>FFV (μm/s)</td>
<td>33.2 ± 1</td>
<td>22.8 ± 1</td>
<td>17.9 ± 1</td>
</tr>
<tr>
<td></td>
<td>Porosity (vol.%)</td>
<td>70.4 ± 0.4</td>
<td>69.8 ± 0.6</td>
<td>71.8 ± 0.5</td>
</tr>
<tr>
<td>UA22 (22 vol.%)</td>
<td>FFV (μm/s)</td>
<td>34.9 ± 2</td>
<td>23.1 ± 09</td>
<td>16.6 ± 1</td>
</tr>
<tr>
<td></td>
<td>Porosity (vol.%)</td>
<td>65.7 ± 0.5</td>
<td>65.5 ± 0.5</td>
<td>69.0 ± 0.5</td>
</tr>
<tr>
<td>UA24 (24 vol.%)</td>
<td>FFV (μm/s)</td>
<td>33.9 ± 2</td>
<td>22.7 ± 0.6</td>
<td>18.5 ± 1</td>
</tr>
<tr>
<td></td>
<td>Porosity (vol.%)</td>
<td>61.8 ± 1.0</td>
<td>63.4 ± 0.8</td>
<td>66.7 ± 0.8</td>
</tr>
<tr>
<td>UA26 (26 vol.%)</td>
<td>FFV (μm/s)</td>
<td>33.4 ± 1</td>
<td>25.4 ± 2</td>
<td>19.3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Porosity (vol.%)</td>
<td>58.9 ± 0.3</td>
<td>59.7 ± 0.4</td>
<td>60.5 ± 0.2</td>
</tr>
</tbody>
</table>
Figure 26 shows representative SEM images of sintered Al₂O₃ materials corresponding to different compositions and FFVs. For the UA20 materials, over the FFV range, morphology can be described as lamellar which is characterized by parallel lamella walls, long, elongated pores, and minimal lamellar bridges in between adjacent the walls. The effects of variation of FFV mainly resulted in an increase of lamella wall thickness with the decreasing FFV. The UA22 materials also exhibited microstructural characteristics similar to that observed for UA20 materials. For the UA24 materials, in the relatively high FFV regime, the density of lamellar bridges in between the adjacent lamella walls is observed to have increased to some extent that attributed dendritic features. However, with the decreasing FFV extent of bridging decreased substantially and morphology turned into lamellar type. Similarly, the morphology of the UA26 materials is observed to dendritic at relatively high FFVs, but with the decreasing FFV morphology progressively transitioned to the lamellar structure.

Figure 17: Variation in average porosity ($p_i$) of ice-templated sintered Al₂O₃ materials as a function of average freezing front velocity (FFV) for all the compositions.
Figure 18: SEM micrographs corresponding to the image plane (Figure 22b) revealing the effects of composition (i.e., ceramic content in aqueous suspension) and FFV on the microstructure of ice-templated Al₂O₃ materials. In each image, ice-growth direction is above and below the page.
4.3.2 Direct observation of damage evolution and failure in ice-templated ceramics in correlations to porosity, templated microstructure, and strain rate

Utilizing imaging technique, our intent here is to obtain insights into the global deformation and failure characteristics in ice-templated sintered Al$_2$O$_3$ materials at two different strain rate regimes in correlations to porosity and templated microstructure. The following discussion is based on the observations made from the images which were acquired from the surfaces of the specimens during the compression tests. In the images of deformation corresponding to quasistatic loading, each observed steel platen was placed between the specimen surface and the platen attached to the testing machine. For dynamic loading, incident bar and transmission bar are on the right-hand side and left-hand side, respectively, of the specimen in each image. Speckle pattern was applied on each specimen surface (specimen color is white) for better visualization. To further probe into the deformation behavior of the materials, we estimated lateral strain ($\varepsilon_{\text{lat}}$) from the images, using the diameter of the undeformed specimens as a reference value. As shown schematically in Figure 27, for each image measurements of diameters at three different heights of a specimen were made to calculate average diameter and estimate average $\varepsilon_{\text{lat}}$.

![Figure 19: Schematic illustrating the measurements of diameters at three different locations from each image of the specimen to calculate average diameter for estimation of average $\varepsilon_{\text{lat}}$.](image)


4.3.2.1 Damage evolution and failure characteristics in UA20 materials (porosity: 69-72 vol.%)

Figure 28a shows representative dynamic (strain rate \(~10^3 \text{ s}^{-1}\)) and quasistatic (strain rate \(~10^{-3} \text{ s}^{-1}\)) compressive response of the UA20 materials. Since for the SHPB experimental conditions in this work strain about 0.3 was achieved, stress-strain curves are shown up to that strain. Across the FFV and strain rate regimes, the UA20 materials exhibited a progressive crushing type compressive response. Compressive stress increased with strain up to a maximum (referred to here as peak stress, \(\sigma_p\)), and beyond that progressive type failure resulted in a gradual decrease of stress with the increasing strain. Under dynamic loading, \(\sigma_p\) as well as failure stress in the plateau regime are observed to be considerably greater in comparison to that under quasistatic loading. Figure 28b shows the variation of \(\sigma_p\) with FFV, which reveals a significant strength enhancement under dynamic loading relative to quasistatic loading, particularly at the higher level of FFV.
Figure 20: (a) Representative uniaxial dynamic (strain rate $\sim 10^3$ s$^{-1}$) and quasistatic (strain rate $\sim 10^{-3}$ s$^{-1}$) compressive stress-strain response of UA20 materials. (b) Variation of maximum uniaxial dynamic and quasistatic compressive strength ($\sigma_p$) with average FFV, where solid and hollow symbols denote the dynamic and quasistatic strength values, respectively. Data in red corresponds to dynamic and blue corresponds to quasistatic loading.

Images shown in Figure 29 reveal damage evolution in the UA20 materials with the increasing strain under the quasistatic and dynamic loading conditions. Figures 29a and 29b show damage evolution under the quasistatic and dynamic loading, respectively, in the UA20 materials processed at relatively high FFVs (31-34 μm/s). Whereas, Figure 29c and 29d show damage evolution under the quasistatic and dynamic loading, respectively, in the UA20 materials processed at relatively low FFVs (16-20 μm/s). The corresponding uniaxial compressive stress-strain curves are also included. Under the quasistatic loading (corresponding to low and high FFVs) the UA20 materials deformed relatively homogeneously, and in the plateau regime deformation progressed without exhibiting any evidence of significant macroscopic crack opening.
and propagation. Figures 29a and 29c thus reveal that under quasistatic loading damage evolution in the UA20 materials was of localized nature and global compressive load-bearing capacity was maintained even beyond the initiation of brittle fracture. Eventually, in the stress plateau regime some fragments (almost parallel to loading direction) started to come out of the specimen (image #3 and image #4) and the process continued with the increasing strain until complete crushing of the specimens. A similar damage evolution pattern is observed in the UA20 materials as well under dynamic loading at both high (Figure 29b) and low FFVs (Figure 29d); note comparable stress-strain curves in between the strain rate regimes at all FFVs (Figure 28a). Damage evolution and failure in the UA20 materials were also observed to be similar at the intermediate FFVs under dynamic and quasistatic loading. Therefore, irrespective of the strain rate regime and FFV, the UA20 materials exhibited relatively homogeneous deformation response. Upon reaching peak stress, materials were able to sustain the applied compressive load and maintained global load-bearing capacity. Therefore, from the direct visualization of damage evolution, we can affirmatively state that the origin of progressive crushing type failure is that there was no macroscopic crack evolution in materials in the vicinity of peak stress, and subsequent to peak stress damage evolved only in the form of minimal fragmentation that gradually increased with the increasing strain.
Figure 21: Images at different strains revealing the characteristics of deformation and failure behavior of UA20 materials processed at relatively high FFV regime at (a) quasistatic and (b) dynamic regimes of strain rates. Similarly, Figures 29c and 29d reveal the characteristics of deformation and failure behavior of UA20 materials processed at relatively low FFV regime at quasistatic and dynamic regimes of strain rates, respectively. Corresponding stress-strain curves are also shown. Red arrow denotes the surface regions of macroscopic damage evolution.
While our earlier studies showed that at a comparable level of porosity $\sigma_p$ under quasistatic loading increased to some extent with the increasing FFV [24,25,28,42], this work revealed a similar behavior under dynamic loading as well (Figure 28b). While damage evolution patterns were not considerably different across the strain rate regimes, higher $\sigma_p$ and plateau stress under dynamic loading in comparison to that under quasistatic loading strongly suggest an enhanced resistance in the UA20 materials to compressive deformation at high-strain rates. Figure 30a shows the variation of $\varepsilon_{\text{lat}}$ with the axial strain ($\varepsilon_a$, obtained from stress-strain curves) for dynamic and quasistatic loading corresponding to the UA20 materials processed at relatively high and low FFVs. Lateral strain measurements were performed until the deformation state where the specimens were still relatively intact (Figure 30b). At lower FFVs, it seems that $\varepsilon_{\text{lat}}$ is comparable across the strain rate regimes. Whereas, at higher FFVs $\varepsilon_{\text{lat}}$ is greater under quasistatic loading compared to that under dynamic loading. Also, at any comparable level of $\varepsilon_a$, the UA20 materials corresponding to higher FFVs consistently exhibited lower $\varepsilon_{\text{lat}}$ under high-strain rate loading compared to that under low-strain rate loading. Lower $\varepsilon_{\text{lat}}$ under dynamic loading (particularly at higher FFVs) can be considered as an indicator of greater resistance in the UA20 materials to compressive deformation at high-strain rates compared to that at low-strain rates. Recall from Figure 28b that strength enhancement in the UA20 materials under dynamic loading was significantly greater at higher FFVs. Therefore, while Figure 29 revealed similar patterns of damage evolution in the UA20 materials irrespective of the FFV and strain rate regime, lateral strain measurements suggest that resistance to deformation in the materials processed at higher FFVs was greater under dynamic loading relative to quasistatic loading.
Figure 22: (a) Variation of $\varepsilon_{lat}$ with $\varepsilon_a$ for dynamic and quasistatic loading corresponding to UA20 materials processed at relatively high and low FFVs. (b) Representative final images of UA20 materials used for $\varepsilon_{lat}$ measurements until the deformation state of material is relatively intact. Left and right halves represent high and low FFV respectively. Upper and lower halves represent the high-strain rate and low-strain rate respectively.

4.3.2.2 Damage evolution and failure characteristics in UA22 materials (porosity: 65-69 vol.%)  

Figure 31a shows representative dynamic (strain rate $\sim 10^3$ s$^{-1}$) and quasistatic (strain rate $\sim 10^{-3}$ s$^{-1}$) compressive response of the U22 materials. The overall characteristic of compressive response of the UA22 materials is similar (progressive crushing type failure) to that of the UA20 materials and did not vary appreciably across the FFV and strain rate regimes. The increase of strength from the UA20 to UA22 materials is attributed to the decrease in porosity, which is a characteristic of porous solids [95]. Both $\sigma_p$ and plateau stress in the UA22 materials were strongly
influenced by the variations of FFV and strain rate, where strength increased significantly with the increasing FFV and strain rate. Figure 31b shows that $\sigma_p$ increased with FFV, but the effect was drastic under dynamic loading. Therefore, a combination of high FFV (material processing condition) and high-strain rate (mechanical loading condition) resulted in a marked enhancement of compressive strength in ice-templated ceramics in the porosity range of 65-72 vol.%. 

Figure 23: (a) Representative uniaxial dynamic (strain rate $\sim 10^3$ s$^{-1}$) and quasistatic (strain rate $\sim 10^{-3}$ s$^{-1}$) compressive stress-strain response of UA22 materials. (b) Variation of maximum uniaxial dynamic and quasistatic compressive strength ($\sigma_p$) with average FFV, where solid and hollow symbols denote the dynamic and quasistatic strength values, respectively. Data in red corresponds to dynamic and blue corresponds to quasistatic loading.

Figures 32a and 32b reveal damage evolution with increasing strain under the quasistatic and dynamic loading, respectively, in the UA22 materials processed at relatively high FFVs (35-38 $\mu$m/s). Similarly, Figures 32c and 32d reveal damage evolution with increasing strain under the
quasistatic and dynamic loading, respectively, in the UA22 materials processed at relatively low FFVs (14-17 μm/s). For each condition (FFV, strain rate), the corresponding stress-strain curve is also included. For each loading condition, the UA22 materials processed at high FFVs exhibited a relatively sharp drop in stress upon reaching peak stress. Figure 32a shows significant fragmentation in the material (right-hand side in image #3) and the formation of macroscopic cracks parallel to the loading direction. With further deformation, more cracks parallel to the loading direction opened up (image #4) and entire specimen tilted with respect to the loading direction, which indicates a significant loss of compressive load-bearing capacity. Under dynamic loading where a significant drop in stress is also observed beyond peak stress (Figure 32b), at comparable strain level UA22 material was able to sustain a greater level of stress relative to that under the quasistatic loading. This is also evident from the dynamic deformation characteristics observed in Figure 32b. While macroscopic crack opening (parallel to loading direction) in the specimen is evident at peak stress level (image #2), with further deformation crack opening and damage evolution were limited (image #3) unlike to that observed under quasistatic loading (Figure 32a). Although more damage accumulation occurred at a later stage of dynamic deformation (image #4), the specimen did not exhibit any tilting with respect to the loading direction. Rather than dynamic damage evolution was progressive crushing type, and damage accumulated through the opening of more number of cracks parallel to the loading direction and lateral expansion of the specimen. Therefore, although the UA22 materials processed at high FFVs exhibited similar stress-strain curves at both strain rate regimes, direct visualization revealed the underlying differences of damage evolution with respect to strain rate. Not only the UA22 materials exhibited considerable strengthening under dynamic loading in comparison to quasistatic
loading, but also dynamic damage was significantly less severe relative to quasistatic damage at comparable strains.

**Figure 24:** Images at different strains revealing the characteristics of deformation and failure behavior of UA22 materials processed at relatively high FFV regime at (a) quasistatic and (b) dynamic regimes of strain rates. Similarly, Figures 32c and 32d reveal the characteristics of
deformation and failure behavior of UA22 materials processed at relatively low FFV regime at quasistatic and dynamic regimes of strain rates, respectively. Corresponding stress-strain curves are also shown. Red arrow denotes the surface regions of macroscopic damage evolution.

Thus, under dynamic loading, the UA22 materials exhibited greater resistant to compressive deformation relative to that under quasistatic loading. For the UA22 materials processed at low FFVs, damage evolution under quasistatic loading (Figure 32c) was similar to that of the materials processed at high FFV (Figure 32a); at both FFV regimes, the UA22 materials exhibited significant structural instability upon reaching peak stress. Dynamic damage evolution was similar at low FFV (Figure 31d) and high FFV (Figure 32b), and it can be affirmatively stated that dynamic damage was significantly less severe compared to quasistatic damage, irrespective of FFV.

Figure 33a shows the variation of $\varepsilon_{lat}$ with $\varepsilon_a$ under dynamic and quasistatic loading, corresponding to the UA22 materials processed at relatively high and low FFVs. A general observation from Figure 33a is that compared to quasistatic loading the UA22 materials were able to sustain compressive load up to a greater level of axial strain under dynamic loading and thus exhibited greater lateral strain, which supports the higher structural stability of the materials at high-strain rates as revealed by the imaging process (Figure 32).
Figure 25: (a) Variation of $\varepsilon_{lat}$ with axial strain for dynamic and quasistatic loading corresponding to UA22 materials processed at relatively high and low FFVs. (b) Representative final images of UA22 materials used for $\varepsilon_{lat}$ measurements until the deformation state of material is relatively intact. Left and right halves represent high and low FFV respectively. Upper and lower halves represent the high-strain rate and low-strain rate respectively.

4.3.2.3 Damage evolution and failure characteristics in UA24 materials (porosity: 61-66 vol.%) 

Figure 34a shows representative dynamic (strain rate $\sim 10^3$ s$^{-1}$) and quasistatic (strain rate $\sim 10^{-3}$ s$^{-1}$) compressive response of the UA24 materials. Under the quasistatic loading, material processed at high FFV failed in a catastrophic manner. Whereas failure response was relatively progressive crushing type for the materials processed at low FFVs. In contrast, dynamic failure response was progressive crushing type irrespective of FFV. While Figure 34b shows that both
dynamic and quasistatic $\sigma_p$ increased with the increasing FFV, at comparable FFVs $\sigma_p$ values are observed to be similar across the strain rate regimes.

Figures 35a and 35c reveal the variations in damage evolution under quasistatic loading at high and low FFVs. At high FFV (Figure 35a), upon reaching peak stress level (image #2), damage evolution in the material caused immediate loss of compressive load-bearing capacity that is evident from tilting of the entire specimen with respect to compression direction (image #3). Whereas, at low FFV (Figure 35c) damage also evolved upon reaching peak stress; however, the specimen was able to withstand the applied load and macroscopic cracks parallel to loading direction evolved progressively. Eventually, the specimen started to tilt at higher strain level (image #4). In the dynamic regime, both at high and low FFVs (Figures 35b and 35d), damage initiation can be observed in the vicinity of peak stress (image #2 in Figures 35b and 35d). However, the specimen did not immediately lose load-bearing capacity which is evident in image #3 in Figures 35b and 35d. While damage continued to evolve beyond peak stress, the UA24 materials were intact up to a certain strain level and irrespective of FFV exhibited a prominent stress plateau under dynamic loading. Eventually, at the higher strain level, dynamic damage became severe (image #4 and image #5 in Figures 35b and 35d) that resulted in a significant drop in compressive stress.
Figure 26: (a) Representative uniaxial dynamic (strain rate $\sim 10^3 \text{ s}^{-1}$) and quasistatic (strain rate $\sim 10^{-3} \text{ s}^{-1}$) compressive stress-strain response of UA24 materials. (b) Variation of maximum uniaxial dynamic and quasistatic compressive strength ($\sigma_p$) with average FFV, where solid and hollow symbols denote the dynamic and quasistatic strength values, respectively. Data in red corresponds to dynamic and blue corresponds to quasistatic loading.
Figure 27: Images at different strains revealing the characteristics of deformation and failure behavior of UA24 materials processed at relatively high FFV regime at (a) quasistatic and (b) dynamic regimes of strain rates. Similarly, Figures 35c and 35d reveal the characteristics of deformation and failure behavior of UA24 materials processed at relatively low FFV regime at quasistatic and dynamic regimes of strain rates, respectively. Corresponding stress-strain curves are also shown. Red arrow denotes the surface regions of macroscopic damage evolution.
Figure 36a reveals the variation of \( \varepsilon_{\text{lat}} \) with \( \varepsilon_a \) under dynamic and quasistatic loading conditions, corresponding to the UA24 materials processed at relatively high and low FFVs. The trend in the variation of \( \varepsilon_{\text{lat}} \) with \( \varepsilon_a \) under dynamic and quasistatic loading for the UA24 materials is similar to that of the UA22 materials. Thus, compared to quasistatic loading the UA24 materials sustained compressive load up to a greater axial strain level under dynamic loading (i.e., greater structural stability), resulting in higher lateral strain.

**Figure 28:** (a) Variation of \( \varepsilon_{\text{lat}} \) with axial strain for dynamic and quasistatic loading corresponding to UA24 materials processed at relatively high and low FFVs. (b) Representative final images of UA24 materials used for \( \varepsilon_{\text{lat}} \) measurements until the deformation state of material is relatively intact. Left and right halves represent high and low FFV respectively. Upper and lower halves represent the high-strain rate and low-strain rate respectively.
4.3.2.4 Damage evolution and failure characteristics in UA26 materials (porosity: 58-61 vol.\%)

Figure 37a shows representative dynamic (strain rate ~$10^3$ s$^{-1}$) and quasistatic (strain rate ~$10^3$ s$^{-1}$) compressive response of the UA26 materials. Under both loading conditions, materials exhibited a significant decrease of $\sigma_p$ with the decreasing FFV. Failure under quasistatic loading was catastrophic, except at low FFV. Whereas, relatively progressive crushing type failure is observed under dynamic loading. Figure 37b shows that the UA26 materials at comparable FFVs exhibited similar $\sigma_p$ irrespective of strain rate. The series of images shown in Figure 38a well support that under quasistatic loading material failed in a completely catastrophic manner. Up to peak stress specimen is observed to be almost intact (image #2 in Figure 38a), but upon reaching peak stress significant damage evolution (image #3) resulted in a drastic loss of load-bearing capacity. For quasistatic loading and at low FFV (Figure 38c), beyond peak stress, a large macroscopic crack (parallel to loading direction) evolved (image #3) but the specimen exhibited a stress plateau regime up to ~0.1 strain (image #4). Beyond this strain, severe damage evolution (image #5) caused loss of load-bearing capacity. In the dynamic regime, at both high and low FFVs (Figures 38b and 38d) damage initiation in the UA26 materials is evident in the vicinity of peak stress (image #2 in Figures 38b and 38d). However, upon reaching peak stress, materials did not immediately loss dynamic load-bearing capacity. With the continuation of dynamic loading damage evolved in the form of cracks parallel to loading direction and the specimens were relatively intact up to a certain strain level, which resulted in the stress plateau regime. Eventually, more cracks parallel to the loading direction evolved in the specimen that resulted in a significant loss of compressive load-bearing capacity. Lateral strain measurements (Figures 39) revealed a trend similar to that observed for the UA22 and UA24 materials. Therefore, compared to
quasistatic loading the UA26 materials sustained compressive load up to greater axial strain level under dynamic loading (i.e., greater structural stability), which resulted in higher lateral strain.

Figure 29: (a) Representative uniaxial dynamic (strain rate ~10^3 s⁻¹) and quasistatic (strain rate ~10^{-3} s⁻¹) compressive stress-strain response of UA26 materials. (b) Variation of maximum uniaxial dynamic and quasistatic compressive strength (σ_p) with average FFV.
**Figure 30:** Images at different strains revealing the characteristics of deformation and failure behavior of UA26 materials processed at relatively high FFV regime at (a) quasistatic and (b) dynamic regimes of strain rates. Similarly, Figures 38c and 38d reveal the characteristics of deformation and failure behavior of UA26 materials processed at relatively low FFV regime at quasistatic and dynamic regimes of strain rates, respectively. Corresponding stress-strain curves are also shown. Red arrow denotes the surface regions of macroscopic damage evolution.
Figure 31: (a) Variation of $\varepsilon_{lat}$ with axial strain for dynamic and quasistatic loading corresponding to UA26 materials processed at relatively high and low FFVs. (b) Representative final images of UA26 materials used for $\varepsilon_{lat}$ measurements until the deformation state of material is relatively intact. Left and right halves represent high and low FFV respectively. Upper and lower halves represent the high-strain rate and low-strain rate respectively.

4.4 Discussion

In this section, first, we summarized (Figure 40) the characteristics of the compressive mechanical response of ice-templated sintered Al$_2$O$_3$ materials in terms of strength range and failure type (progressive crushing vs. catastrophic) based on the dependence on composition, FFV, and strain rate. For this purpose, Figure 40 is divided into four quadrants: (i) quadrant 1 – low solids loading and low FFV, (ii) quadrant 2 – high solids loading and low FFV, (iii) quadrant 3 – low solids loading and high FFV, and (iv) quadrant 4 – high solids loading and high FFV. Here, the low and high solids loadings are considered as the composition range of 20–22 vol.% and 24–
26 vol.%, respectively. Similarly, the low and high FFV regimes correspond to 15–20 μm/s and 32–38 μm/s, respectively. Additionally, each quadrant is divided into two segments: low-strain rate and high-strain rate. As a result of the variations of composition, FFV, and strain rate, $\sigma_p$ values are observed to reside within a wide range with the lowest and highest strength values of 4 and 113 MPa, respectively. Therefore, we also categorized $\sigma_p$ values into three empirical strength groups: low strength (<10 MPa), medium strength (approximately 10–50 MPa), and high strength (approximately >50 MPa).

**Figure 32:** Summary of variation in compressive strength and deformation behavior of ice-templated sintered porous Al$_2$O$_3$ ceramics at different solids loadings, FFV and strain rate regimes.
Left and right halves represent low and high solids loading respectively. Upper and lower halves represent the low and high FFV respectively.

In quadrant 1 (low solids loading, low FFV), compressive response evaluated at the low-strain rate regime is characterized by very low strength (4–7 MPa, low strength range) and progressive crushing failure. However, $\sigma_p$ (10–15 MPa, medium strength range) is enhanced at high-strain rates, but the deformation pattern remains progressive crushing type. Thus, we can state that in quadrant 1 the effect of strain rate is mainly on strength. In quadrant 2 (high solids loading, low FFV), materials exhibited an increase of strength with $\sigma_p$ values residing within a relatively broad range of 9–28 MPa (medium strength range). The strength enhancement is attributed to the decrease of porosity and possibly changes in microstructure (Figure 35). Materials exhibited mixed compressive deformation response. For $\sigma_p$ closer to lower-bound (9 MPa) deformation pattern is progressive crushing type but changed to catastrophic type for $\sigma_p$ closer to upper-bound (28 MPa). Materials corresponding to the same composition exhibited considerable strain rate sensitivity with $\sigma_p$ residing within the range of 18–50 MPa (medium strength range). Additionally, under dynamic loading, all the materials failed in a progressive crushing manner. In quadrant 3 (low solids loading, high FFV), while composition range is the same as in quadrant 1, a slight decrease in porosity (66-71 vol.%) was measured relative to that in quadrant 1 (69–73 vol.%), which is attributed to increase in FFV and associated changes in microstructure (Figure 26). In this quadrant, both quasistatic (10–23 MPa, medium strength range) and dynamic (18–43 MPa, medium strength range) $\sigma_p$ values were higher in comparison to the respective ones corresponding to quadrant 1, supporting the strong influence of both FFV and strain rate on compressive response. However, the deformation pattern leading to failure remained the same (progressive crushing) across quadrants 1 and 3. In
quadrant 4 (high solids loading, high FFV), while composition range is the same as in quadrant 2, a substantial decrease in porosity (58–62 vol.%) was measured relative to porosity in quadrant 2 (61–66 vol.%), which is attributed to increase in FFV and associated changes in microstructure (Figure 26). In this range, $\sigma_p$ enhanced significantly under both quasistatic (40–95 MPa, high strength range) and dynamic (70–113 MPa, high strength range) loading relative to the respective ones in quadrant 2. However, in quadrant 4, the compressive response is in sharp contrast across strain rate regimes; materials exhibited catastrophic failure under quasistatic loading whereas progressive crushing failure under dynamic loading. Therefore, Figure 40 reflects on the complexity of compressive deformation behavior in ice-templated ceramics due to the intertwined dependence on porosity, microstructure, and strain rate. Figure 40 can be viewed as design guidelines to synthesize ice-templated ceramics of targeted porosity and microstructure with respect to desired mechanical performance under dynamic and quasistatic compressive loading conditions.

Our previous work sheds some light on the porosity and strain rate dependence of uniaxial compressive mechanical properties in ice-templated porous ceramics [55]. Whereas, the present results revealed the underlying processes of damage evolution and failure, and how they are strongly influenced by porosity, microstructure, and strain rate regime. While compressive stress-strain signatures reflect on the influence of different parameters to mechanical properties, this study provides significant insights into the origin of the differences of compressive deformation behavior in between the dynamic and quasistatic loading conditions, in correlations to porosity and microstructure, based on the direct observation of damage evolution and failure. Direct observation of failure is important for improved understanding of macroscopic signature of the compressive mechanical response of ice-templated ceramics. Our study revealed that the
signatures in the compressive stress-strain curves of ice-templated ceramics do not necessarily provide complete insights of deformation behavior; direct observation is crucial to probe into the failure mechanisms and address the structure-mechanical property relationships.

Damage evolution and failure type in ice-templated ceramic materials are observed to depend strongly on porosity. In the quasistatic strain rate regime of compressive loading, materials at high porosity (~70 vol.%) exhibited progressive crushing failure. Imaging process revealed that irrespective of FFV and strain rate, mechanisms of damage evolution remained similar (Figure 29). Upon reaching peak stress, cracks parallel to loading direction developed and more cracks evolved with the increasing strain. This damage evolution mechanism did not lead to an abrupt drop in stress and thereby resulted in failure by progressive crushing. Recall that the UA20 materials exhibited lamellar morphology with the negligible density of lamellar bridges over the FFV range (Figure 26). In our previous study [55], we discussed that in higher porosity (~70 vol.%) ice-templated Al₂O₃ materials thin lamella walls are prone to fracture by buckling induced elastic instability, which results in localized failure and direct evidence to that is provided by the current results (Figure 29). The lack of lamellar bridges also allows the lamellar structure to expand laterally with relative ease, i.e., lamella walls can separate without experiencing any appreciable resistance, resulting in the formation of cracks parallel to the loading direction. The morphology remained the same across the FFV regime, and hence the damage evolution and failure mechanism.

Under the quasistatic loading, at any strain level, the extent of damage is observed to be severe in the material processed at lower FFV compared to that processed at higher FFV, which supports the measured strength enhancement with the increasing FFV. Experimental studies further revealed a significantly lesser extent of damage under dynamic loading compared to under quasistatic loading at comparable FFV. This work thus showed that the origin of dynamic strength
enhancement in the UA20 materials is directly related to the greater resistance in the materials to brittle fracture under dynamic loading compared to quasistatic loading. Particularly, very little damage is observed under dynamic loading in the UA20 material processed at higher FFV (Figure 29b) compared to quasistatic loading (Figure 29a), which can be attributed to the measured significant dynamic strength enhancement at higher FFVs (Figure 28b).

Under dynamic loading conditions, micro-inertia effects in cellular solids become dominant and attribute to the strain rate sensitivity of mechanical properties [110–114]. The micro-inertia effects in brittle cellular solids can influence the collapse of cell walls at the onset of compressive fracture as well as during the progressive deformation in stress plateau regime, leading to a stress enhancement for failure initiation and/or propagation under high-strain rate loading conditions. Particularly, strength enhancement due to the micro-inertia effects can be significant when an asymmetric mode of deformation such as buckling is associated with the deformation behavior of cellular solids [115,116]. The lateral inertia of cell walls can suppress the cell wall deformation by buckling and result in macroscopic dynamic stress enhancement due to continued axial compression of cell walls before the asymmetric mode of deformation is triggered [115]. Therefore, it is possible that the micro-inertia effects delayed the initiation of elastic instability within lamella walls of ice-templated sintered Al₂O₃ materials of higher porosity and resulted in dynamic $\sigma_p$ being higher than quasistatic $\sigma_p$. Note that Figure 29 revealed that the UA20 material was well intact up to a higher uniaxial compressive stress level under dynamic loading compared to quasistatic loading. Under dynamic loading, micro-inertia effects could also delay the buckling-induced fracture of lamella walls during the progressive crushing stage and enhance stress in the plateau regime. As it is evident from Figure 29 that the extent of damage evolution in the stress plateau regime was significantly less under dynamic loading compared to quasistatic loading.
With the decreasing porosity, the effects of FFV on damage evolution and failure became significant and hence the macroscopic response, particularly under the quasistatic loading. At lower FFVs, progressive crushing type failure resulted from the damage evolution mechanism that we discussed earlier in this section. Whereas, at higher FFVs, with the decreasing porosity failure under quasistatic loading became typical brittle type. Image analysis revealed that indeed up to peak stress level materials were intact, whereas upon reaching peak stress significant amount of damage evolved within the large volume fraction of material causing complete loss of compressive load-bearing capacity, which can be evidenced from the tilting of the specimens with respect to the loading direction as well as by the slippage of the platens (Figures 35a, 38a). Therefore, at lower porosity, ice-templated materials became stronger with increasing FFV but the accumulated elastic strain energy under compression could have been high enough to cause abrupt failure under quasistatic loading. The sudden evolution of damage in the vicinity of peak stress supports the post-mortem analysis that revealed axially split large fragments in the low porosity materials (UA24, UA26).

Under dynamic loading greater structural stability of the low porosity materials compared to quasistatic loading is clearly evident, irrespective of FFV. Materials did not experience any abrupt loss of compressive load-bearing capacity, because damage evolution under dynamic loading was significantly limited as few cracks parallel to the loading direction developed in the vicinity of peak stress. Beyond peak stress, materials expanded laterally with the formation of more cracks parallel to the loading direction while still carrying the applied load, which resulted in stress plateau regime unlike to that under quasistatic loading. The compressive stress-strain response of ice-templated Al₂O₃ materials is consistent with the strain-softening compressive response of materials (referred to as Type II structures) which are significantly more prone to micro-inertia
based strength enhancement under dynamic loading in comparison to the structures that exhibit a flat-topped stress-strain curve in the plateau regime (referred to as Type I structures) [115,117]. In Type II structures, dynamic strength enhancement in the plateau regime is associated with the micro-inertia led resistance to an asymmetric mode of deformation such as buckling. As revealed by the imaging process in this work, a lesser extent of damage evolution under dynamic loading is in support that failure by elastic buckling of lamella walls in ice-templated ceramic materials is significantly resisted at high-strain rate loading conditions.

4.5 Summary

1. The current study investigated the effects of porosity, microstructure, and strain rate regime on the damage evolution and failure under uniaxial compressive loading in ice-templated sintered Al$_2$O$_3$ materials. The porosity of the materials was varied by systematically changing the ceramic volume fraction of aqueous suspensions. For each composition, freezing front velocity (FFV) was varied to modify microstructure while maintaining comparable porosity across the microstructures.

2. Compressive response of the materials was investigated both in the dynamic (strain rate \(\sim 10^3 \text{ s}^{-1}\)) and quasistatic (strain rate \(\sim 10^{-3} \text{ s}^{-1}\)) loading regimes. High-strain rate experiments were performed using an SHPB set up. For direct observation of damage evolution and failure, a FASTCAM SA4, Photron camera was employed for both types of compression tests.

3. Porosity of the sintered materials was found to be in the range of 58-72 vol.%. Microstructural analysis revealed that in the high porosity regime, morphology was lamellar. In the lower porosity materials processed at higher FFVs morphology was dendritic but transitioned to lamellar structure with decreasing FFV. The systematic variation of porosity and microstructure
allowed to investigate the corresponding effects on damage evolution and failure in ice-templated ceramics across two very different strain rate regimes.

4. For each composition, $\sigma_p$ increased with FFV at both strain rate regimes. Interestingly, in the higher porosity materials (UA20, UA22) strength enhancement under dynamic loading was significant in the materials processed at high FFVs. On the other hand, for lower porosity materials (UA24, UA26), dynamic and quasistatic $\sigma_p$ remained comparable at any specific FFV.

5. Under quasistatic loading, the UA20 materials (porosity: 69-72 vol.%) deformed in a progressive crushing manner without exhibiting any evidence of significant macroscopic crack opening and propagation. Damage evolution mechanism under dynamic loading remained similar. The origin of progressive crushing type failure was observed to be the absence of macroscopic crack evolution in the vicinity of peak stress, and subsequent to peak stress damage evolved only in the form of minimal fragmentation that gradually increased with increasing strain. However, at any comparable level of strain, the extent of damage was less under dynamic loading compared to quasistatic loading, which suggests enhanced resistance to brittle fracture at high-strain rates. The experimental observations were further correlated with the micro-inertia effects. The damage evolution and failure process in the UA22 materials (porosity: 65-69 vol.%) under both loading conditions is observed to be similar to that in the UA20 materials.

6. However, with the decreasing porosity damage evolution process changed, particularly under quasistatic loading condition and for the materials (UA24, UA26) processed at higher FFVs. Image analysis revealed that up to peak stress level materials were intact, whereas upon reaching peak stress, significant amount of damage evolved within the large volume fraction of material causing complete loss of compressive load-bearing capacity, which was also evident from the tilting of the specimens with respect to the loading direction.
7. In the UA24 (porosity 61-66 vol.%) and UA26 (porosity 58-61 vol.%) materials, damage evolution under dynamic loading in the vicinity of peak stress was limited and damage accumulation occurred progressively with increasing strain, which strongly supports the greater structural stability in ice-templated ceramic materials at high-strain rates. The observed dynamic behavior is consistent with the Type II porous structures, where micro-inertia effects cause strength enhancement in the plateau regime by increasing the resistance to an asymmetric mode of deformation such as buckling.

8. The experimental observations were further rationalized with the measurements of the evolution of lateral strain (quantified from image analysis) with axial strain as a function of porosity, microstructure, and strain rate.

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CHAPTER 5

ROLE OF MICROSTRUCTURE ON IMPACT RESPONSE AND DAMAGE MORPHOLOGY OF ICE-TEMPLATED POROUS CERAMICS

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5.1 Introduction

Impact events, where a stationary object and a flying object or two flying objects interact, are routinely encountered in various applications, ranging from aerospace to military. In these events, materials and structures are subjected to inelastic deformation and failure under high rate loading conditions [118–123]. Understanding the deformation behavior of materials during the projectile-target interactions and the correlation between mechanical properties and impact
performance of materials is of profound fundamental interest. The complexity of impact behavior of materials stems from that the projectile-target interactions are affected by various parameters, such as the type of target and projectile material (ceramic, metal, polymer, composite), the shape of the impactor, projectile velocity, and loading configuration (ranging from normal to oblique impact) [124–128]. Most of the fundamental studies on the impact behavior of materials in the open literature are, however, focused on characterizing the interactions between a metal impactor and a ceramic target, because of the specific relevance in designing ceramic armor systems. The design of a ceramic armor system varies significantly, ranging from lightweight body armor to heavy-duty vehicle armor. An armor system is typically comprised of multiple layers of materials, with each layer having a specific role in defeating an incoming projectile [54,129–131]. In general, a frontal ceramic plate (due to high hardness and compressive strength) resists the penetration of a projectile and aids in eroding and decelerating the projectile. Whereas, a thick polymer composite layer behind the ceramic layer attributes energy-absorption ability to the armor system and can arrest the rest of the projectile if it was not completely defeated by the frontal ceramic layer. There is also interest in porous solids for armor systems, such as using as a backing material layer [118,130,132–134]. Under compressive loading (a dominant stress state in an impact event), porous solids can undergo progressive deformation, absorb energy, delay stress wave propagation, and attenuate stress waves [95,99,135,136], which could be beneficial to improve the performance of ceramic armor systems and make the systems lightweight.

To use porous solids in impact and related applications, it is essential to understand both the impact response of the materials and the correlations between high-strain rate mechanical properties and impact behavior. Although there are numerous fundamental studies on the impact behavior of ceramic materials, such studies on porous ceramics remain sparse. This investigation
thus focuses on sphere impact response of ice-templated porous ceramics and dynamic mechanical property-performance relationships in these materials. The ice-templating technique enables the fabrication of hierarchical ceramics with a directional pore morphology [17,24,25,137]. These materials are fabricated via unidirectional solidification of aqueous ceramic suspensions. In these materials, three primary microstructural features are lamella walls, directional pores, and lamellar bridges. The parallel ceramic lamella walls are separated by directional pores, and lamellar bridges connect the adjacent lamella walls. Ice-templated microstructure is highly tunable and the variation in microstructure greatly affects the compressive strength of these materials [29,55,138].

This study has three specific aims. The first aim is to investigate the role of microstructure on the impact deformation behavior of ice-templated sintered alumina (Al$_2$O$_3$) materials. To develop ice-templated materials with different microstructure, during the ice-templating step, we fabricated materials at different freezing front velocities (FFVs). In ice-templated ceramics, both lamella wall thickness and overall pore size increase along the growth direction of ice crystals, resulting in a structural gradient. Thus, the second aim of this study is to evaluate the influence of the direction of impact, relative to the growth direction of ice crystals, on the impact response of these materials. The third aim is to assess the impact behavior of ice-templated materials in correlation to their mechanical property. Among various mechanical properties, the uniaxial compressive strength of ceramics is inherently related to their impact behavior [121,125,126]. Therefore, we characterized the uniaxial compressive response of ice-templated sintered Al$_2$O$_3$ materials under high-strain rate loading conditions to understand the influence of microstructure on the dynamic compressive strength. From these three aims, we addressed the role of ice-templated microstructure on the dynamic mechanical property-performance relationship. In this study, Al$_2$O$_3$ is used as a model material, and the results apply to other ceramic materials as well.
5.2 Experimental

5.2.1 Fabrication of ice-templated ceramics

Aqueous ceramic suspensions (26 vol.% solid loading) were prepared from a commercially available ultrafine $\alpha$-Al$_2$O$_3$ powder, $d_{50} = 300$ nm (APA-0.5, Sasol, Tuscan, AZ). Using a custom-made device [19], aqueous Al$_2$O$_3$ suspensions were ice-templated at three different FFV regimes: low FFV, moderately-high FFV, and very-high FFV. A special design of the cold-finger was used to achieve very-high FFV. To enable uniform dispersion of Al$_2$O$_3$ particles in deionized (DI) water, 1 wt.% (of powder) anionic dispersant (Darvan-C, R.T. Vanderbilt Co, Norwalk, CT) was used. The suspensions were ball milled for 24 hours using zirconia (ZrO$_2$) spheres of diameter 5 mm, followed by an additional 1 hour of milling after mixing of 5 wt.% of the binder (poly-(2-ethyl-2-oxazoline)) to each suspension. The suspensions, after separating the milling media, were de-aired under a low vacuum for 30 min. The processed suspensions were next utilized for ice-templating.

In this device, a Teflon mold is placed on a thin (thickness 0.8 mm) copper (Cu) plate (referred to here as “Cold-finger”) and then the mold is filled with an aqueous ceramic suspension. In this work, a Teflon mold of inner dimensions 25.4 mm x 25.4 mm x 18 mm was utilized and the was filled up to 16 mm in height with suspension. Next, the suspension in the mold is solidified under the influence of the unidirectional temperature gradient. For this purpose, the entire assembly is inserted inside liquid nitrogen (N$_2$) Dewar and placed above the surface of liquid N$_2$. Once the temperature of Cold-finger reaches below 0 °C, the ice crystals start to nucleate at the bottom of suspension in contact with Cold-finger and grow vertically under the influence of the thermal gradient. Thermal insulation surrounding the outside of the Teflon mold ensures a unidirectional thermal gradient. By adjusting the distance between the Cold-finger and liquid N$_2$, the unidirectional freezing front velocity (FFV, growth rate) of the ice crystals is controlled.
Materials were ice-templated at gaps of 1 mm and 30 mm between the Cold-finger and liquid N$_2$. To achieve higher FFV, another Cold-finger was designed in which two vertical Cu strips were attached at the bottom of the Cold-finger. During ice-templating process using this Cold-finger, a gap of 1 mm was maintained between the Cold-finger and liquid N$_2$ surface. However, the Cu strips were immersed in N$_2$ which allowed achieving significantly greater FFV. Thus, the materials were processed at different FFVs which allowed to study the effects of both microstructure and microstructure gradient on sphere impact response of ice-templated materials of comparable porosity. The frozen samples were freeze-dried at a pressure of 0.014 mbar and temperature of -54°C inside a freeze dryer (2.5 L, Labconco, Kansas City, Missouri) for 96 hours. The freeze-dried samples were heated at 450°C for 4 hours to burn out the organic binder and sintered at 1550°C for 4 hours in a box furnace (KSL-1700X, MTI Corporation, Richmond, CA) in the air atmosphere.

5.2.2 Characterization of porosity and microstructure

The sintered samples were of dimensions of 21 mm x 21 mm x 13 mm, where 13 mm being the height of the samples in the growth direction of ice crystals. For each sintered sample, 1.5 mm thin layer from both top and bottom were removed, leaving the final average dimensions at 21 mm x 21 mm x 10 mm. The density of the porous sintered materials ($\rho^*$) was determined from the measurements of mass and dimensions, whereas relative density ($\rho_r$) was calculated as $\rho_r = \rho^*/\rho_s$, taking bulk density $\rho_s$ of Al$_2$O$_3$ as 3.96 g/cm$^3$. Total porosity was estimated as $p_t = (1 - \rho_r) \times 100$. To characterize any variation of porosity within each large sample, for each FFV regime, one large sample was sectioned into two halves. Several small specimens were extracted from each half (Figure 41a) and used to calculate $\rho_r$ and $p_t$ (Figure 42). A desktop Phenom scanning electron microscope (SEM) was employed for microstructure characterization. A few specimens from the materials fabricated at very-high FFV were also characterized using a ZEISS
Xradia 510 versa 3D X-ray microscope (XRM) system, with specimen dimensions were approximately 10 mm x 10 mm x 2.4 mm, and the pixel size used was 1.26 µm.

For each representative freezing condition (i.e., FFV), three specimens each of 2.5 mm thickness were extracted from 1 large sample as shown schematically in Figure 41b, which were utilized to characterize the variation of microstructure along the growth direction of ice crystals. Note that SEM images were obtained from the planes which were perpendicular to the growth direction of ice crystals. From each image plane 5 SEM images were captured corresponding to five different locations, and the images were utilized for estimation of lamella wall thickness ($t$). The microstructure characterization was carried out using an open-source application FIJI ImageJ. A pre-processing manual correction was performed for brightness and contrast. Further the images were processed with plugin “Trainable Weka Segmentation” to segment into ceramic lamella walls (bright area) and pores (dark area). These segmented images were utilized in quantification of $t$.

**Figure 33:** (a) Schematic denoting the sectioning of sintered material into two halves and extracting smaller specimens along each half sections. (b) Schematic representing the planes employed for SEM imaging along the ice-growth direction. The sintered material (10 mm along
height) was sectioned into three halves at 3.3 mm using diamond saw to extract a section each of 2.5 mm.

**Figure 34:** Variation of porosity ($p_t$) as a function of FFV. Green circles denote porosity of the sintered samples. The porosity values of extracted specimens from the top and bottom halves are indicated by red triangles and blue inverted triangles, respectively.

### 5.2.3 Characterization of sphere impact response

Figure 43a shows a schematic of the custom-made impact test setup that consists of a compressed air powered gas gun, sabot, and sample holder. In this device, the sabot carrying a steel sphere (impactor) is loaded into the pressurized gas gun, and on opening the pressure release valve, the sabot accelerates down the barrel toward the sample. The sabot is made of ABS plastic and contains a ceramic magnet inside, which enables to hold the steel sphere in place while the sabot travels toward the stopper plate. For the impact studies in this work, S2 tool steel spheres of
diameter 4.7 mm were utilized, with a new sphere for each test. In the test setup, an aluminum (Al) stopper plate is placed at the end of the barrel to stop the sabot, which forces the steel sphere to eject from the sabot. Now, this steel sphere travels through the center hole of the stopper plate and impacts the ceramic material placed in the sample holder. The sample holder, made from Al, is a two-part fixture, where an Al enclosure that holds the sample rests on an Al backing plate. Both the Al enclosure and backing plate are held together with metal screws. The sample is inserted inside the Al enclosure, and to support the sample inside the enclosure, ballistic clay surrounds all four sides of the sample, as an interface between the enclosure and sample. This arrangement allows for the safe recovery of the samples after the impact tests. A thin layer of petroleum jelly is applied to reduce friction between the back surface of the sample and the backing plate. All the sphere impact studies were performed at a velocity of about 80 m/s.

Figure 35: (a) Schematic of a custom-made impact test device. The inset on left shows a two-part sample holder made from aluminum (Al), where an Al enclosure that holds the sample rests on an Al backing plate. Both the Al enclosure and backing plate are held together with metal screws. The inset on right shows the plastic sabot with a magnet inserted inside to hold a steel sphere (impactor) at the front of the sabot. Each impact event was imaged using a high-speed camera,
which was placed at angle relative to the impact direction. (b) Schematic showing that thin sections were removed from the top and bottom surfaces to obtain a sintered sample of 10 mm height for impact test. (c) Each extracted sintered material was either impacted on the top surface (opposite to the growth direction of ice crystals) or bottom surface (in the growth direction of ice crystals) with a steel sphere.

Figure 43b schematically shows that each impact sample was obtained after removing a thin layer (1.5 mm) from both the top and bottom of the sintered material. Black speckle pattern was applied on the top and bottom surfaces of each sample for better visualization of damage during impact. Each ice-templated sintered sample was either impacted on the bottom surface (Figure 43c) or top surface (Figure 43d). We refer sphere impact on the bottom surface as an impact along the growth direction of ice crystals, whereas the impact on the top surface as an impact opposite to the growth direction. For each FFV regime and direction of impact, on an average, five samples were tested. Each impact event was captured using A FASTCAM SA4, Photron camera with imaging speed of 100,000 frames per second (fps, 10 μs interval between successive images), and resolution of 192 × 128 pixels. The camera was placed at an angle to the direction of impact. Few tests were also performed, where the camera was placed perpendicular to the direction of impact. Post impact, the recovered samples were characterized for impact crater radius ($R$), mass loss (ML), and depth-of-penetration (DOP). ML for each sample was determined by subtracting the sample mass measured after impact from the sample mass measured before impact, and ML represents the mass ejected during impact. DOP was measured using a Vernier caliper. Damage in impacted specimens was characterized using SEM.
5.2.3.1 Imaging of sphere impact perpendicular to impact direction

In few tests, the impact events were imaged perpendicular to the direction of impact. The schematic of the experimental setup is shown in Figure 44. The goal of this experimental configuration was to characterize the depth-of-penetration of impactor during the three phases of impact. Further, the instantaneous DOP information was used to evaluate the impactor velocity during the penetration phase ($V_p$), and rebound phase ($V_r$). The average values of $V_p$ and $V_r$ were used to estimate the average kinetic energy (KE) of the impactor in the penetration phase (KE$_p$) and rebound phase (KE$_r$). While the average kinetic energy (KE) of the impactor at the beginning of impact was estimated from the impactor velocity, $V_i$. The following equations were used to estimate KE$_i$, KE$_p$, and KE$_r$. Where $m$, being the mass of impactor.

$$KE_i = \frac{1}{2}mV_i^2$$  \hspace{1cm} (1) \\
$$KE_p = \frac{1}{2}mV_p^2$$  \hspace{1cm} (2) \\
$$KE_r = \frac{1}{2}mV_r^2$$  \hspace{1cm} (3)
5.2.4 Split-Hopkinson pressure bar (SHPB) testing

To characterize the uniaxial compressive response of ice-templated sintered Al$_2$O$_3$ materials under high-strain rate loading conditions (>10$^2$/s), a split-Hopkinson pressure bar (SHPB) set up was used. From each 21 mm x 21 mm x 10 mm large sample, three specimens each of 10 mm x 10 mm x 2.5 mm were extracted and tested using the SHPB. The SHPB setup consists of a gas gun chamber, solid striker bar of length 330.2 mm, a solid incident bar of length 1524 mm, and a solid transmission bar of length 914.4 mm. All the bars are made of high-strength Al alloy each with a diameter of 19.05 mm. Figure 45 shows the schematic representation of the three specimens extracted from different heights (bottom, middle, top) along the ice-growth direction of ice crystals for the dynamic compression tests.

For each test, a specimen was sandwiched in between the incident bar and the transmitted bar. The striker bar on impact with incident bar generates a compressive elastic stress pulse which travels along the incident bar and applies a uniaxial compressive load on the specimen. A portion
of the stress pulse transmits through the specimen to the transmitted bar while the rest of the pulse reflects back to the incident bar. The transmitted and reflected stress pulses (captured through strain gages) are utilized to calculate stress and strain and strain rate, respectively, in the material. For each representative freezing condition, three specimens each of 10 mm x 10 mm x 2.5 mm were extracted along the ice-growth direction and utilized for the SHPB tests. Since longitudinal elastic stress wave propagation speed is significantly reduced in materials with high porosity (i.e., low impedance) compared to the counterpart bulk solid materials [1], Al alloy bar was utilized (instead of high strength maraging steel) to reduce impedance mismatch between the bar material and ice-templated sintered ceramic material, which facilitates transfer of elastic stress wave through specimen to transmission bar.

For testing of ceramic materials, it is important to achieve stress equilibrium in the elastic deformation regime prior to brittle fracture [2]. During the planar impact between metal striker bar and incident bar, elastic stress wave of trapezoid form develops that has a steep rise time of loading stress. To achieve stress equilibrium in ceramic specimens before fracture, pulse shaping technique is commonly utilized to increase the rise time of the loading pulse [3]. In this work, for each SHPB experiment, a copper (Cu) pulse shaper was placed at the striker bar-incident bar interface to increase the rise time of the loading pulse. Figure 46a shows incident stress pulses without and with Cu pulse shaper. With the presence of Cu pulse shaper rise time was significantly enhanced compared to the loading pulse without the pulse shaper and high-frequency noises were removed.

For testing of ceramic materials employing SHPB setup, a general requirement is that there should be 3-5 wave transits within a specimen to achieve force balance (i.e., equilibrium) before macroscopic failure in the material [2]. Longitudinal wave speed \( C_s \) in a solid is estimated as

\[
C_s = \sqrt{\frac{E_s}{\rho_s}},
\]  

(4)
where $E_s$ and $\rho_s$ are Young’s modulus and density of the material, respectively [4]. As will be discussed later, porosity ($\rho^*$) in the ice-templated sintered Al$_2$O$_3$ materials varied with both composition and FFV. Table 1 shows $C_s$ of the sintered materials as a function of composition and freezing condition (i.e., the gap between Cold-finger and liquid N$_2$). $E_s$ was determined from the slope of the initial regime of the elastic part of the quasistatic stress-strain curve. Transit time ($t_s$) for the leading edge of an incident wave to travel through a specimen is given by

$$t_s = \frac{l_s}{C_s},$$

(5)

where $l_s$ is the length of the specimen. From Table 4, it can be seen that single transit time within the materials varied in between 2-7 $\mu$m, depending on the composition and freezing condition (Cold-finger gap). Figure 46a shows that the rising part of an incident pulse is about 60 $\mu$s, which would ensure that there will be several wave reflections in the specimens before reaching peak stress.

Stress pulses were measured through the strain gages (mounted in the middle of the incident and transmission bars) using a signal conditioning amplifier (2310B, Vishay) and a high-speed digitizer (NI PCI-5105, National Instrument). In this work, the universal general-purpose strain gages of linear pattern (CEA-13-250UW-350) type were utilized for the measurements of stress waves. Stress in a specimen is estimated as [5]

$$\sigma(t) = E \varepsilon_T(t) \frac{A_t}{A_s},$$

(6)

where $E$ is Young’s modulus of the bar material, $\varepsilon_T(t)$ is the time-resolved axial strain in the transmission bar, and $A_t$ and $A_s$ are the cross-sectional areas of the transmission bar and sample, respectively. Similarly, strain rate in a specimen is calculated as [5]

$$\dot{\varepsilon}(t) = -\frac{2C_0}{l_s} \varepsilon_R(t),$$

(7)
where $C_o$ is the wave velocity of the bar material, $l_s$ is the original length of the specimen, $\varepsilon_R(t)$ is the time-resolved axial strain of the reflected pulse in the incident bar. Finally, strain in a specimen is calculated as [5]

$$\varepsilon(t) = \int_0^t \dot{\varepsilon}_R(t).$$

(8)

Figure 46b shows the representative incident, reflected and transmitted signals measured from an ice-templated sintered porous Al$_2$O$_3$ specimen. Whereas, Figure 46c shows a comparison of the forces acting on the specimen from the incident end and transmitted end of the SHPB setup corresponding to the signals shown in Figure 46b, which suggests that stress equilibrium was achieved in the material prior to macroscopic failure.

**Table 4:** Variation of longitudinal wave speed ($C_s$) and single transit time ($t_s$) in the specimens extracted from different heights along the ice-growth direction of ice-crystals as a function of FFV

<table>
<thead>
<tr>
<th>FFV</th>
<th>Location of extracted specimen</th>
<th>Bottom</th>
<th>Middle</th>
<th>Top</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very-high</td>
<td>Wave speed, $C_s$ (m/s)</td>
<td>1710.9</td>
<td>1599.9</td>
<td>1281.9</td>
</tr>
<tr>
<td></td>
<td>Transit time, $t_s$ (µs)</td>
<td>1.5</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Moderately-high</td>
<td>Wave speed, $C_s$ (m/s)</td>
<td>1265.0</td>
<td>1186.4</td>
<td>933.3</td>
</tr>
<tr>
<td></td>
<td>Transit time, $t_s$ (µs)</td>
<td>2.4</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Low</td>
<td>Wave speed, $C_s$ (m/s)</td>
<td>833.7</td>
<td>690.5</td>
<td>636.1</td>
</tr>
<tr>
<td></td>
<td>Transit time, $t_s$ (µs)</td>
<td>3.6</td>
<td>4.3</td>
<td>4.7</td>
</tr>
</tbody>
</table>
**Figure 37:** Schematic representation of the three specimens extracted from different heights (bottom, middle, top) along the ice-growth direction of ice crystals for the dynamic compression tests.

**Figure 38:** (a) Modification of incident signal with the use of copper pulse shaper, (b) Representative strain gage signals obtained from the modified SHPB set-up of very-high FFV material, (c) Comparison of forces acting on the incident end and transmitted end of modified SHPB set-up for a very-high FFV material.
Figure 39: Distribution of lamella wall thickness ($t$) along the growth direction of ice crystals (planes 1-4) of sintered samples processed at (a) low FFV (13.8 μm/s), (b) moderately-high FFV (26.1 μm/s), and (c) very-high FFV (76.03 μm/s).
Figure 40: Distribution of pore major axis ($a$) along the growth direction of ice crystals (planes 1-4) of sintered samples processed at (a) low FFV (13.8 µm/s), (b) moderately-high FFV (26.1 µm/s), and (c) very-high FFV (76.03 µm/s).
Figure 41: Distribution of pore minor axis ($b$) along the growth direction of ice crystals (planes 1-4) of sintered samples processed at (a) low FFV (13.8 µm/s), (b) moderately-high FFV (26.1 µm/s), and (c) very-high FFV (76.03 µm/s).
5.3 Results

5.3.1 Porosity, microstructure, and structural gradient

Ice-templated materials were fabricated at three different FFV regimes: very-high FFV (76.1 ± 6.6 µm/s), moderately-high FFV (28.8 ± 1.5 µm/s), and low FFV (13.1 ± 0.8 µm/s). Figure 42 shows the variation of porosity in the sintered samples with FFV. Also, included are the data corresponding to the specimens extracted from the top and bottom halves of the sintered samples. Note that for each FFV regime, the extracted specimen data corresponds to the small specimens obtained from a single sintered material. In the sintered samples, \( p_t \) exhibits a gradual decrease with the increase in FFV. Whereas, the variation of \( p_t \) corresponding to the top and bottom halves with FFV reveals the influence of FFV on the variation of porosity within the samples. In each FFV regime, a considerable difference in porosity is observed between the top half and bottom half, with the former being considerably more porous compared to the latter. Also, the porosity difference increased significantly with a decrease in FFV, from about 3.3 % to 9.7 %. Interestingly, at each FFV, the porosity of the sintered samples is observed to be closer to the porosity of the bottom half, suggesting that a portion of the top of the sample was significantly more porous compared to the rest of the sample.

Figure 50 shows representative SEM images corresponding to the four image planes (Fig. 41b), revealing the variation of microstructure in the sintered materials with FFV and along the growth direction of ice crystals (i.e., variation within a sample). Morphology of the material corresponding to low FFV is highly lamellar throughout the material volume, characterized by large elongated pores. We can observe a significant increase in lamella wall thickness along the growth direction of ice crystals. The material corresponding to moderately-high FFV also exhibits
lamellar morphology with an increase in wall thickness along the growth direction. However, the structure is finer compared to the material processed at low FFV. The microstructure of the material processed at very-high FFV is even finer and the morphology is referred to as dendritic due to the enhanced lamellar bridge density, particularly in the bottom regions (a high-magnification SEM image is shown in Figure 51b). Figure 51 shows three-dimensional (3D) reconstructed XRM images of a very-high FFV material, for which specimens were extracted from the bottom and top regions. From the XRM images, we can observe that the bottom half has a significantly finer microstructure compared to the top half.

Thus, the microstructural analysis revealed a strong influence of FFV on microstructure, and in each FFV regime, microstructure changed significantly along the growth direction of ice crystals. The structural gradient in ice-templated ceramics is a consequence of the continuous change in the growth velocity of ice crystals during the unidirectional solidification process. During ice-templating, ice crystals nucleate on the freezing surface and grow upward under the influence of the applied gradient. With distance, growth velocity decreases, the thickness of crystals increases, and some of the crystals grow at the expense of the others. This, in turn, results in a continuous increase of lamella wall thickness and pore size along the growth direction and development of a structural gradient.
Figure 42: Representative SEM images along the ice-growth direction corresponding to image planes 1-4 of a sintered sample processed at (a-d) low FFV (13.8 µm/s), (e-h) moderately-high FFV (26.1 µm/s), and (i-l) very-high FFV (76.1 µm/s). Note plane 1 corresponds to the bottom surface and plane 4 corresponds to the top surface.
Figure 43: (a) Specimens for XRM were extracted from bottom and top regions. (b) A high-magnification SEM image of the bottom region, revealing enhanced density of lamellar bridges and highly dendritic microstructure. Three-dimensional (3D) reconstructed XRM images of (c) bottom region and (d) top region.

Figure 44: Variation of (a) lamella wall thickness, $t$, (b) pore major axis, $a$, (c) pore minor axis, $b$, and (d) pore aspect ratio, $\chi_p$, with FFV and along the growth direction of ice crystals.
Figure 52 shows the variation of average lamella wall thickness, $t$, pore major axis, $a$, pore minor axis, $b$, and pore aspect ratio, $\chi_p$, with FFV and along the growth direction of ice crystals. Distribution plots of these parameters are shown in Figures 47-49. With the increase in FFV, all the parameters exhibit a significant decrease, whereas the parameters also exhibit an increase along the growth direction. The low FFV materials have the highest average $t$, $a$, and $b$ of 24.4 $\mu$m, 207.6 $\mu$m and 15.5 $\mu$m, respectively. Whereas, the very-high FFV materials have the lowest average $t$, $a$, and $b$ of 4 $\mu$m, 6.75 $\mu$m, and 2.47 $\mu$m, respectively. The average $t$, $a$, and $b$ along the growth direction increased by 40.6 %, 43.4 %, and 29.8 % in the low FFV materials, by 57 %, 49.4 %, and 69.7 % in the moderately-high FFV, and by 79.4 %, 73.3 %, and 52.7 % in the very high FFV. Thus, all the materials exhibit a structural gradient along the growth direction.

5.3.2 Sphere impact response

For each FFV regime, we discussed the response of the materials for sphere impact on the top surface (impact direction opposite to growth direction) and bottom surface (impact along the growth direction). Optical images extracted at different times ($\mu$s) from high-speed videos are shown in Figure 53. The images are also representative of the impact behavior of the materials of the corresponding FFV regimes. Each image at $t = 0$ approximately corresponds to the start of the impact event where the impactor (steel sphere) made the first contact with the sample. An arrow on an image pointing toward the sample implies that the impactor was traveling toward the material, whereas an arrow pointing outward suggests that the sphere was traveling in the opposite direction. Times shown on the images corresponding to the 4th column were when the sphere was completely out of the material. A significant amount of Al₂O₃ debris that came out from the specimens, due to brittle damage, caused a level of difficulty in pinpointing the exact time frame when the impactor was completely out of the sample. Each image in column 5 shows the impacted
surface of the recovered sample, whereas the image in column 6 shows the back surface of that sample.

5.3.2.1 Ice-templated materials processed at very-high FFVs (76.1 ± 6.6 μm/s)

Figures 53a and 53b show the snapshots of the impact events for top surface impact and bottom surface impact, respectively, on the materials that were fabricated at very-high FFV. For an impact on the top surface, the penetration process started as soon as the impactor (steel sphere) was in contact with the material, suggesting that kinetic energy (KE) of the projectile was high enough to instantly overcome the resistance of the porous network. But the impactor was able to only partially penetrate the material, which could be attributed to the loss of KE of the steel sphere and/or an increased resistance of the material ahead of the projectile. At about 30 μs, penetration into the material ceased, and the impactor came to a halt. However, the sphere rebound did not start immediately and a dwell phase evolved, that lasted for about 30 μs, during which the high-speed video did not indicate any movement of the impactor. At about 60 μs, the sphere started to travel backward, and by 240 μs was completely out of the sample. The impact caused the formation of a crater on the sample surface. Some of the samples exhibited the formation of macroscopic cracks on the impact surface, which are referred to as radial cracks. While we observed radial cracks in the high-speed videos, we were unable to detect those cracks in the extracted still images. But radial cracks were visible in the recovered samples. Only in some of the samples, cracks propagated all the way to the back surface, and it appears that radial cracks were more pronounced at the back surface.

For the impact on the bottom surface, the impactor came to a halt within 10 μs, and by 120 μs the sphere was completely out of the sample. Thus, the total duration of impact (120 μs) was
considerably shorter compared to the impact opposite to the growth direction. Another difference is that severe radial cracking occurred on the impact surface, and all the samples exhibited radial cracks at the impact and back surfaces.

Analysis of high-speed images indicates that the radial cracks on the impact surface evolved during the dwell phase. Figure 54 shows a series of optical images for a sample that was impacted along the growth direction, which reveal that the radial cracks evolved during the dwell phase on the impact surface. Cracks emerged from the region of impact and propagated radially, while the sphere was in constant contact with the ceramic. However, no further radial crack formation and/or extension occurred on the impact surface after the dwell phase.

5.3.2.2 Ice-templated materials processed at moderately-high FFVs (28.8 ± 1.5 μm/s)

Figures 53c and 53d show the snapshots of the impact events on the top surface and bottom surface, respectively, of ice-templated materials that were fabricated at moderately-high FFVs. For both directions of impact, the general sequence of the events is comparable to that observed in very-high FFV samples and thus not discussed further. However, the time taken for the sphere to come to a halt was slightly longer, the sphere rebound time was longer, and the total duration of impact was significantly longer in these samples compared to that in the very-high FFV samples. The extent of the damage (crater diameter) for the top surface impact is observed to be greater compared to the bottom surface impact. And, the extent of damage in these samples is observed to be greater compared to that in the very-high FFV samples. Some of the samples also exhibited radial cracks, and the propensity of radial cracking is observed to be greater for impact along the growth direction.
5.3.2.3 Ice-templated materials processed at low FFVs (13.1 ± 0.8 μm/s)

Figure 53e and 53f show the snapshots of the impact events on the top surface and bottom surface, respectively, of materials that were fabricated at low FFVs. Clearly, the impact crater size is significantly greater in these materials. The time taken by the sphere to come to a stop, the sphere rebound time, and the total duration of impact increased further compared to the materials of other FFV regimes. Some of the samples exhibited radial cracking, and the propensity of radial cracking was greater for impact along the growth direction.
**Figure 45:** Optical images from high-speed videos revealing the interactions between steel sphere (impactor) and ice-templated sintered Al₂O₃ materials. Very-high FFV materials: (a) top surface impact, i.e., impact direction was opposite to the growth direction of ice crystals and (b) bottom surface impact, i.e., impact direction was along the growth direction. Moderately-high FFV
materials: (c) top surface impact and (d) bottom surface impact. Low FFV materials: (e) top surface impact and (f) bottom surface impact. In these tests, imaging was performed at an angle to the direction of impact. “Sphere contacts” – means that the impactor just touched the sample surface and beginning of penetration phase. “Sphere stalls” – refers to the start of dwell phase. “Sphere rebound” – end of dwell phase and beginning of rebound phase. “Sphere exits” – end of rebound phase and the impactor is not in contact with the sample surface. Also shown are the post-impact images of impacted surface and back surface of the samples.

**Figure 46:** Optical images from high-speed video revealing the evolution of radial cracks on the impact surface during the dwell phase in the ice-templated material fabricated at very-high FFV. Impact direction was along the growth direction of ice crystals. In this test, imaging was performed at an angle to the direction of impact.
Figure 47: Percentage of occurrence of radial cracks on impact surface and back surface for impact direction (a) opposite to and (b) along the growth direction of ice crystals. For each direction of impact, also shown is the percentage of samples that were recovered intact.

In Figure 55, we have summarized the percentage of the samples that exhibited radial cracks (number of samples showed radial cracks/total number of samples tested) and the percentage of the samples that were recovered intact (number of samples recovered intact/total number of samples tested) relative to the FFV regime and the direction of impact. Here intact means that despite the impact-induced damage, a sample was recovered in one piece. The most prominent trend is that all the very-high FFV samples exhibited the development of radial cracks for impact along the growth direction. Radial cracks propagated all the way through for most of the samples, and only 20% of the samples were recovered intact. Whereas, for the impact direction opposite to the growth direction, 50% of the samples exhibited radial cracks on the impact surface but only 20% on the back surface, which suggests that in only some of the samples, the crack propagated all the way through the sample. As a result, 83% of the samples were recovered intact.
In the moderately-high FFV materials, 67% of the samples showed the development of radial cracks on both surfaces for impact along the growth direction, but only 20% for impact opposite to the growth direction. For impact along the growth direction, 83% of the samples were recovered intact, whereas all the samples were intact for impact opposite to the growth direction. In the low FFV samples, 80% of the samples exhibited radial cracks on both impact and back surfaces for impact along the growth direction. Whereas, for impact opposite to the growth direction, 40% of the samples exhibited radial cracks on the impact surface and 60% on the back surface. 40% and 100% samples were intact for impact along and opposite to the growth direction, respectively. Therefore, we can state that ice-templated materials are more prone to radial cracking for impact along the growth direction of ice crystals compared to opposite to the growth direction. Irrespective of the FFV regime, 80 – 100% of samples were intact for impact direction opposite to the growth direction. Thus, the results suggest that both microstructure and the direction of impact strongly influence the impact response of ice-templated porous ceramics. We emphasize that Figure 55 is not a complete impact performance indicator, since the radius of damage crater, depth-of-penetration, and mass loss was not considered here (discussed later).

From the analysis of high-speed videos, we identified three distinct phases of impact in ice-templated porous materials: a penetration phase (equivalent to loading phase) where the impactor continues to penetrate the material, a dwell phase where the impactor remains in contact with the material without further penetration, and a rebound phase (equivalent to unloading phase) where the impactor is projected outward from the material. Figure 53 reveals a strong influence of FFV on the duration of the penetration and rebound phases (discussed further in the next section). To further confirm the three phases, in a few tests, the impact events were imaged perpendicular to the direction of impact, Figure 56. The direction of impact was opposite to the growth direction.
The optical images clearly reveal the three phases of impact, as well as the difference in the extent of penetration with FFV. For the very-high FFV material, the steel sphere barely penetrated the material, whereas almost completely went inside of the material fabricated at low FFV and was projected out during the rebound phase. For the moderately-high FFV material, the steel sphere penetrated about half of the sphere diameter. Figure 56 also shows that the ceramic debris that came out of the materials during impact was maximum in the low FFV material.

**Figure 48:** Optical images from high-speed videos showing the positions of steel sphere (impactor) during the penetration, dwell, and rebound phases of impact for the materials fabricated at (a-d) very-high FFV, (e-h) moderately-high FFV, and (i-l) low FFV. Impact direction is opposite
to the growth direction of ice crystals. In these tests, imaging was performed perpendicular to the direction of impact.

In the experimental configuration where we imaged perpendicular to the impact direction, we were also able to capture crack propagation in one of the very-high FFV samples. Note that only one of the sample surfaces was imaged, and cracks would appear only if they developed on that surface. Figure 57 shows a series of optical images, which reveals crack propagation on the surface that was imaged for a very-high FFV sample for impact direction along the growth direction. Cracks emerged in the direction of impact and propagated toward the back surface (left to right). It appears that cracks might have developed between two frames shown in Figure 57b and Figure 57c (note 10 µs time interval between two successive images for imaging speed at 100 fps), thus during the dwell phase. While the cracks appeared during the dwell phase, they continued to grow even during the rebound phase. We suggest that these are radial cracks. Figure 54 reveals that the radial cracks developed on the impact surface and development of radial cracks on the impact surface were completed within the dwell phase. Figure 57, however, suggests that the radial cracks continued to develop in the interior of the sample during the rebound phase (unloading phase) and propagated toward the other end of the sample.
Figure 49: Crack propagation on the side surface in a very-high FFV material for impact direction along the growth direction of ice crystals.

Figure 58a shows the variation of impact crater radius ($R$) with FFV for both directions of impact. Recall that the sphere radius was 4.7 mm. $R$ decreased significantly with FFV and is observed to be higher for top surface impact compared to bottom surface impact, particularly in the low and moderately-high FFV samples. Figures 58b and 58c show the variation of mass loss (ML) and depth of penetration (DOP) with FFV, respectively. The average sample mass and height were 7.54 g and 10 mm, respectively. With the increasing FFV, both ML and DOP decreased substantially; however, the measurements do not suggest a clear trend on the influence of the direction of impact. The maximum ML and DOP, which occurred in the low FFV materials, is about 4.4% of sample mass and 48.3% of sample height, respectively. Thus, the DOP was more significant compared to ML. Whereas, the minimum ML and DOP, which occurred in the very-high FFV materials, is only 0.2% of sample mass and 15.5% of sample height, respectively. The results in Figure 58 further confirm the strong influence of FFV on impact response and that penetration resistance of materials increased with FFV. Recall from Figure 42 that with the increase in FFV porosity only marginally decreased. Thus, the results inevitably suggest the vital
role of templated microstructure in impact response. However, the influence of the direction of impact appears to be insignificant for ML and DOP.

![Figure 50](image)

**Figure 50**: Variations of (a) impact crater radius ($R$), (b) mass loss (ML), and (c) depth-of-penetration (DOP) with FFV.

The above results revealed that the ice-templated microstructure exhibits a strong effect on the impact response, with the direction of impact mainly influencing radial cracking and radius of damage crater. The materials developed at the very-high FFV regime showed the maximum resistance to penetration, but the resistance to penetration deteriorated significantly with the decreasing FFV. Microstructure variation also influenced the duration of different phases (discussed in the next section).

### 5.3.3 Duration of penetration phase, dwell phase, and rebound phase

Figure 59 shows the variation of the duration of penetration phase ($t_p$), dwell phase ($t_d$), and rebound phase ($t_r$) with FFV. $t_p$ is the time taken for steel impactor to come to a halt on the
ceramic surface and $t_r$ is the time taken after the dwell phase for the impactor to come back to the initial point of contact, i.e., the position where the impactor made the first contact with specimen surface. Thus, for both $t_p$ and $t_r$, the distance traveled by the impactor for a given sample was the same. The results do not reveal any clear influence of the direction of impact on these durations. The trend of $t_d$ vs. FFV is not clear, but it appears that there is a decrease in $t_d$ with FFV. We can also state that $t_d$ for very-high FFV materials was smaller compared to that of the materials of other FFV regimes. On the other hand, with the increase in FFV, both $t_p$ and $t_r$ decreased significantly, which we attribute to the increased impact resistance in the materials with FFV. The greater the resistance of a porous ceramic structure, the smaller is the DOP, and hence sooner the impactor comes to a halt. As mentioned above, for both $t_h$ and $t_r$, the distance traveled by the impactor is the same, but for each sample $t_r$ is significantly greater than $t_p$, which suggests that the average velocity ($V_r$) of the impactor in the rebound phase is significantly smaller than the average velocity in the penetration phase ($V_p$). The decrease in $t_r$ with FFV is simply related to the smaller distance the impactor had to travel backward with the increasing FFV (smaller DOP).

One interesting finding of this study is the existence of a dwell phase. Although the current results do not indicate any clear trend on the effects of FFV and the direction of impact on the dwell period, all the materials exhibited a dwell phase. Dwell is a well-known phenomenon that occurs during the projectile-ceramic target interactions, which refers to the duration when the impactor is in constant contact with a dense (i.e., non-porous) ceramic target and exerting pressure and inducing damage into the ceramic but penetration into the target has not begun [139]. During dwell, through the induced damage, penetration resistance of the target is overcome, and penetration commences if the projectile was not already completely consumed within the dwell period. In ice-templated ceramics, penetration began immediately, and a dwell phase evolved at
the end of the penetration phase and ended when the rebound phase commenced. Analysis of high-speed videos suggests that impact crater developed prior to the beginning of the dwell phase, whereas radial cracks evolved during the dwell phase, and crack extension across the sample thickness continued to occur during the rebound phase as well.

**Figure 51**: Influence of FFV on the duration of (a) penetration phase, $t_p$, (b) dwell phase, $t_d$, and (c) rebound phase, $t_r$.

### 5.3.4 Impactor velocity in the penetration phase and rebound phase

From the analysis of the high-speed videos that were captured perpendicular to the impact direction, we determined the position of an impactor (referred to as DOP) with time during the penetration phase and rebound phase. Note that for each FFV regime, only a few samples were tested where the imaging direction was perpendicular to the impact direction. Figure 60a shows the variation of DOP with time for very-high FFV, moderately-high FFV, and low FFV materials. The maximum DOP values in Figure 60a are consistent with the DOP measurements after the tests.
(Figure 60c). A linear fit of the variation of DOP with time during penetration and rebound phases was performed to determine the average $V_p$ and $V_r$, respectively. Figure 60b shows the variation of average $V_p$ and $V_r$ with FFV. All the materials were impacted at about the same velocity, $V_i$ (~80 m/s). Irrespective of the maximum DOP and time taken during the penetration and rebound phases, the average $V_p$ and $V_r$ are observed to be almost independent of FFV. Thus, while ice-templated microstructure has a pronounced influence on $R$, ML, DOP, radial cracking, and duration of penetration and rebound phases, the effect of microstructure on average impactor velocity during the penetration and rebound phases is observed to be insignificant. Figure 60b also suggests that compared to $V_i$ (80 m/s), average $V_p$ dropped in the range of 40 – 50 m/s, suggesting a significant loss of KE (about 40 – 50%) during the penetration phase which was mostly spent in inducing brittle damage in the materials. Note that $V_p$ is an average over the entire duration of impact, whereas impactor velocity at the beginning of the penetration phase was 80 m/s but became zero at the end of the phase. Also, the lower the FFV, the greater is the DOP and the duration of the penetration phase. Thus, Figure 60b suggests that during the penetration phase, the rate of decrease of impactor velocity (i.e., deceleration) is less sensitive to microstructure variation. Average $V_r$ is even lower (< 10 m/s) than average $V_p$. The average $V_r$ can be used to estimate residual KE of the impactor. Figure 60c shows the variation of average kinetic energy (KE) of the impactor in the penetration phase (KE$_p$) and the rebound phase (KE$_r$) with FFV. Impactor KE at the beginning of impact (KE$_i$) was about 1.4 J. Figure 60c suggests that for all the materials, the loss of KE by the impactor is significant, which was spent in causing brittle damage in the materials, and comparable across the FFV regimes.
Figure 52: (a) Variation of (a) depth-of-penetration (DOP) with time for the materials impacted in the direction opposite to the growth direction of ice crystals. (b) Variation of average velocity of the impactor in penetration phase ($V_p$) and rebound phase ($V_r$) with FFV. Impactor velocity ($V_i$) at the beginning of impact was about 80 m/s. (c) Variation of average kinetic energy (KE) of the impactor in the penetration phase (KE$_p$) and rebound phase (KE$_r$) with FFV. Impactor KE at the beginning of impact (KE$_i$) was about 1.4 J.

5.3.5 Impact-induced brittle damage

We investigated both the impact surface, as well as the back surface, to study the impact-induced damage and focused on the differences of damage between the materials fabricated at very-high FFV and low FFV. Figure 61a shows an optical image of the impact surface of the material fabricated at very-high FFV, revealing a damage crater, several concentric, circumferential (within the crater) cracks, and three prominent radial cracks. The direction of impact was along the growth direction of ice crystals. While all the features are characteristic of brittle damage, investigation of any plastic deformation within Al$_2$O$_3$ grains is beyond the scope
of this work. All the radial cracks originated from the region of impact and connected with the circumferential cracks. Figure 61a shows that within each radial crack, there are regions where the crack path is tortuous (b), as well as relatively straight (c). The SEM image in Figure 61b reveals a part of a radial crack that propagated through (almost perpendicular) the lamella walls, resulting in a highly zig-zag crack path. Whereas, the SEM image in Figure 61c reveals a part of a radial crack that propagated parallel to lamella walls, resulting in a relatively straight crack path. In ice-templated ceramics, on a plane perpendicular to the growth direction of ice crystals, multiple domains, each containing a set of parallel lamella walls, are randomly oriented. Therefore, depending on the orientation of the walls relative to the crack path, the crack could be forced to propagate through the walls or parallel to the walls. It appears that crack propagation through the walls is a more difficult and energy-consuming process compared to crack propagation parallel to the walls. The radial cracks propagated all the way to the back surface, Figure 61i. During impact, as the steel sphere tried to penetrate the material, the region ahead of the impactor was separated from the surrounding region and pushed ahead by the impactor, and the process resulted in a circumferential crack. As the process repeated over the course of the penetration, several concentric circumferential cracks developed. Circumferential crack can also be observed on the back surface, and we noticed that the material within the circumferential crack at the back surface was slightly protruded out compared to the rest of the surface. The regions between the circumferential cracks (particularly away from the center) are relatively intact with some small fragments of lamella walls that can be observed, Figure 61(f-g). Whereas, the regions within the central part of the crater (Figure 61d) that were directly beneath the impactor are observed to be highly comminuted, where severe fragmentation of lamella walls to individual grains occurred (Figure 61h).
Figure 53: (a) An optical image of showing an impact crater, several concentric circumferential cracks, and three prominent radial cracks on the impact surface of ice-templated sintered Al$_2$O$_3$ material fabricated at very-high FFV. The material was impacted along the growth direction of ice crystals. (b-h) SEM images revealing fracture characteristics in the material and fragmentation of lamella walls. (b) A radial crack propagated through lamella walls and (c) a radial crack propagated in between lamella walls. (d) Central part and (e) circumferential region of impact crater. (f-g) Fragmentation of lamella walls. (h) Highly pulverized region with lamella walls fragmented to individual grains. (i) An optical image of the back surface of the impacted sample.
Figure 62 shows the damage characteristics in a material that was fabricated at low FFV, and we can observe significant differences of damage characteristics compared to the material that was fabricated at very-high FFV. However, the observed features suggest typical brittle damage. The impact crater was bigger (approximately 350 times larger DOP compared to that in the very high-FFV materials) and hence most of the crater was out of focus in an optical microscope, Figure 62a. The crack path within a radial crack is observed to be relatively straight (region b in Figure 62a), and the crack propagation direction is parallel to the walls, Figure 62b. Unlike the very-high FFV material, concentric circumferential cracks are absent within the impact crater, as well as on the back surface (Figure 62f). Within the impact crater, most of the lamella walls were fragmented into pieces, Figures 62(c-e). However, unlike the very-high FFV material, severe fragmentation of lamella walls to individual grains is observed to be absent.

From the above discussion, we can state that the mechanism of brittle damage evolution during sphere impact is significantly different in the materials fabricated at very-high FFV and low FFV, suggesting the strong influence of microstructure. As we showed in Figure 52, overall pore size is significantly smaller in the very-high FFV materials compared to that in the low FFV materials, and it is known that the strength of ice-templated ceramics increases with the decrease in pore size and aspect ratio [24,25,29,55,137]. Therefore, it is expected that the observed differences in the damage characteristics emerged from the strength variation in the materials across the FFV regimes.

5.3.6 Dynamic compressive strength

Since the impact is a dynamic process of deformation in materials, in this study, we performed SHPB tests to determine dynamic (high-strain rate) compressive strength of materials. We suggest that for impact velocity of 80 m/s, strength evaluated under high-strain loading
conditions is a better representation of the impact resistance of materials compared to strength measured under quasistatic loading conditions. Stress state in materials under impact loading is complex, but uniaxial compressive strength of materials is well related to the impact resistance of materials.

**Figure 54:** (a) An optical image of showing damage on the impact surface of ice-templated sintered Al$_2$O$_3$ material fabricated at low FFV. The material was impacted along the growth direction of ice crystals. (b-e) SEM images revealing fracture characteristics in the material and fragmentation of lamella walls. (b) A radial crack propagated parallel to lamella walls. (c) Central part and (d) circumferential region of impact crater. (e) Fragmentation of lamella walls. (h) Highly
pulverized region with lamella walls fragmented to individual grains. (f) An optical image of the back surface of the impacted sample.

Figure 63 shows dynamic uniaxial compressive stress-strain curves of materials fabricated at different FFV regimes, whereas the variation of maximum compressive strength with FFV is shown in Figure 63. In all the SHPB tests, an engineering strain of about 0.2 was achieved with a strain rate of the order of $10^3$ s$^{-1}$. In each FFV regime and from each sample, three specimens were extracted from different heights (bottom, middle, top) along the growth direction of ice crystals (see Figure 45). Except for the bottom specimens in very-high FFV materials, all other specimens exhibited a continuous brittle crushing failure response. There is a linear regime in stress-strain curves, which is followed by a stress plateau regime, where stress decreases gradually with strain and, in this regime, materials fail by continuous brittle crushing of lamella walls. Figure 64 shows that the compressive strength of the specimens from the very-high FFV materials is higher than the specimens from other the FFV regimes. Also, in the very-high FFV materials, the strength of the bottom specimens is significantly higher than the middle and top specimens. Figure 64 shows that strength decreases from bottom to top, i.e., along the growth direction of ice crystals, and the difference became prominent with the increasing FFV. In each FFV regime, pore size and wall connectivity decreases and increases, respectively, along the growth direction, which increases strength. Similarly, with increasing FFV, overall pore size and wall connectivity decreases and increases, respectively, and hence strength increases with FFV. Figures 63 and 64 reveal that as the increase in FFV has a significant influence on the ice-templated microstructure, so is on the dynamic compressive strength. Thus, the differences that we observe in the impact behavior of the materials across the FFV regimes are inherently related to the variation in the dynamic compressive strength of the materials.
Figure 55: Representative uniaxial dynamic compressive stress-strain curves of materials fabricated at (a) very-high FFV, 54.9 ± 2 μm/s, (b) moderately-high FFV, 25.3 ± 0.5 μm/s, and (c) low FFV, 13.5 ± 0.6 μm/s. For each FFV regime and from each sample, three specimens were extracted from different heights (bottom, middle, top) along the growth direction of ice crystals. Legends with vol.% indicate porosity of specimens.

Figure 56: Variation of maximum dynamic compressive strength of specimens extracted from different heights (along the growth direction of ice crystals) of materials with FFV.
5.4 Discussion

Due to the energy-absorbing ability, porous solids are vital for impact protection and related applications. Although there are numerous studies on the dynamic behavior and impact response of porous metallic and polymeric materials, such studies on porous ceramics remain sparse. The interest in ice-templated ceramics is due to their unique directional porosity and highly tunable microstructure. Also, compressive strength of these materials measured along the growth direction of ice crystals is significantly higher compared to that of open-cell porous ceramics. Our recent studies revealed that the compressive response of these materials is strongly influenced by strain rate regime (quasistatic vs. dynamic), and properties under dynamic loading conditions could improve by about 100% depending on the porosity and morphology [55,68,140,141]. Also, under dynamic loading conditions, these materials exhibit progressive crushing type failure attributing energy-absorbing ability irrespective of porosity and morphology, which is in sharp contrast to their quasistatic response. The findings that ice-templated ceramics exhibit enhanced mechanical properties and progressive crushing type failure behavior under high-strain rate loading conditions are enticing to use these hierarchical materials in dynamic environments and provided a strong motivation for the current study. The central focus of this study is to investigate the influence of microstructure and the direction of impact (relative to the growth direction of ice crystals) on the impact behavior of ice-templated sintered Al₂O₃ materials and understand the relationship between dynamic compressive strength and impact response.

In Figure 65, we summarized the influence of microstructure and the direction of impact on the sphere impact response of ice-templated sintered Al₂O₃ materials. The results revealed that sphere impact behavior and the dynamic compressive response of these materials are strongly influenced by microstructure. During the ice-templating step, the microstructure was modified by
changing FFV. The higher the FFV, the finer is the microstructure (thinner lamella walls, smaller pore size and aspect ratio, and greater connectivity between walls), and dynamic compressive strength increased significantly with FFV. The results revealed a direct relationship between dynamic compressive strength and resistance to penetration. As a result, with the increase in strength, the diameter of damage crater, depth of penetration, and mass loss reduced significantly.

The impact process evolved in three phases: penetration phase, dwell phase, and rebound phase. With the increasing impact resistance of the materials, the duration of these phases (mainly penetration and rebound phases) and hence the total duration of impact decreased significantly. The results suggest that the average velocity during the penetration phase and rebound phase is relatively unaffected by the variation of microstructure. The stronger the material, the smaller is the DOP and hence the duration of penetration and rebound phases. Thus, through the deliberate modification of microstructure, not only the impact resistance of the materials but also the duration of the different phases of impact can be tuned.

The impact crater radius is observed to be higher for top surface impact compared to bottom surface impact. However, for other parameters such as DOP, ML and duration of different phases of impact, the effect of the direction of impact is relatively insignificant. In addition to impact crater (developed during the penetration phase), damage in the materials evolved in the form of radial cracks, and the propensity of radial cracking was higher when impacted along the growth direction of ice crystals. High-speed imaging revealed that radial cracks developed on the impact surface during the dwell phase, and the cracks continued to propagate in the interior of the material even during the rebound phase. The propensity of crack propagation from the impact surface to the back surface was also higher for impact along the growth direction and post-recovery. Thus, most of the very-high FFV samples were split into multiple pieces.
Figure 57: A summary of the influence of microstructure and direction of impact on sphere impact response of ice-templated sintered Al₂O₃ materials. Strength data correspond to SHPB data.

Radial cracking is a common phenomenon that occurs in dense ceramics during projectile-target interactions; however, radial cracks evolve at the back surface of the target. The radial cracks evolve in a thin ceramic target (impactor diameter comparable to plate thickness) due to the bending of the target or in thick ceramic target from the reflected tensile stress waves (compressive stress waves reflected as tensile stress waves from the target – backing metal interface due to impedance mismatch). Once the cracks evolve at the back surface, they propagate toward the front surface. However, in the current study, radial cracks in the porous Al₂O₃ materials developed on
the impact surface and propagated toward the back surface. Chen et al. [141] studied cracking in porous (porosity in the range of 5 – 45 vol.%) solid oxide fuel cell (SOFC) material using the spherical indentation technique (sphere diameter 25 μm). They reported the development of only radial cracks on the surface of indent, the cracks evolved from the boundary of the indented region and propagated on the surface and parallel to the direction of loading in the interior of the material, which is very similar to the observations of the current study. Their finite element analysis suggested that a tensile hoop stress field develops on the surface on loading, and the field increases and expands on unloading, which drives the radial cracks. It is possible that a similar type of stress field caused the formation and propagation of radial cracks during sphere impact in ice-templated materials. An in-depth study is needed, particularly with more imaging perpendicular to the impact direction, to understand the impact velocity dependence of radial cracking, which we will address in a separate study.

The penetration resistance of the materials strongly depended on microstructure (pore size and morphology) and thus on the compressive strength, and the stronger the material the greater was the resistance. The strength variation across the materials of different FFV regimes resulted in a significant difference in the mechanism of damage evolution during impact. In the low FFV material (low strength), upon impact, lamella walls within the contact region crumbled into pieces and collapsed, allowing greater and easier penetration by the impactor. On the other hand, in the very-high FFV material, the lamella walls within the contact region exhibited significant resistance to fracture. Although some of the regions beneath the impactor were heavily fragmented into individual grains, the lamella walls within the damage zone did not crumble into fragments. Due to the significant resistance by the walls, instead, a circumferential crack developed, which caused
part of the material to be pushed ahead by the impactor and allowed penetration, and the processed repeated.

In Figure 66, we compare energy absorption per unit volume ($U_v$), estimated for impact and dynamic compression. To determine $U_v$ for impact, total energy absorbed was estimated by subtracting $KE_r$ from $KE_I$ and the difference was divided by the volume of the impact crater. The calculations were performed for both the top surface and bottom surface impact. For dynamic compression, $U_v$ was estimated from the area of high-strain rate stress-strain curves (up to 0.15 strain), corresponding to the top part and bottom specimens. Figure 66 shows that for both impact and dynamic compression, $U_v$ increased with FFV. $U_v$ values are higher for impact compared to that for dynamic compression. Under impact, in addition to compression, energy is lost through various other mechanisms, such as radial cracking, ceramic debris ejecting out of the sample, and friction between debris and impactor. The purpose of Figure 66 is not to compare the exact values but reveal the similarity in the trend in $U_v$ with FFV for both impact and dynamic compression, further reinforcing the direct relationships between the impact behavior and dynamic compressive response of ice-templated materials.
Figure 58: Variation of energy absorption per unit volume, $U_v$, estimated for impact and dynamic compression.

The overall results suggest that the high FFV materials exhibited the best impact performance, due to the significantly lower DOP, ML, and $R$ and higher $U_v$ compared to that of the other materials. In the high FFV materials, these values improved further for the impact direction along the growth direction compared to the opposite to growth direction. However, these materials suffered from significant radial cracking, and the materials were less intact for the impact along the growth direction. Our results suggest that pore size and wall connectivity can be tuned to significantly influence the impact behavior of ice-templated porous ceramics, providing a design space for developing these materials with the targeted usages in dynamic environments.

5.5 Summary

This study showed that impact response of ice-templated porous materials depends strongly on microstructure and, to some extent, on the direction of impact relative to the growth direction of impact. With the decrease in pore size and increase in connectivity between lamella walls, the
impact resistance of materials increased significantly, which reflected in decreased size of damage crater, depth-of-penetration, and mass loss. Radial cracking also occurred in the materials, and the materials fabricated at very-high FFV showed a greater propensity for radial cracking for impact along the growth direction. It was observed that the entire impact process into the ice-templated materials evolved in three phases, penetration phase, dwell phase, and rebound phase. The analysis of high-speed videos revealed that damage crater developed during the penetration phase, whereas radial cracking evolved during the dwell phase but continued to the extent within the material during the rebound phase. Through the deliberate modification of microstructure, not only the impact resistance but also the duration of the three phases can be tuned. Materials fabricated at very-high FFV and low FFV exhibited significantly different mechanisms of damage evolution during impact. The compressive response of materials was measured under dynamic loading conditions. The results showed a direct relationship between impact response and dynamic compressive behavior of materials. The results of this study revealed that the modification of microstructure of hierarchical porous ceramics can have a profound influence on their dynamic mechanical performance and properties.

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CHAPTER 6

CHARACTERIZATION OF DYNAMIC AND QUASISTATIC COMpressive Mechanical Properties of Ice-Templated ALumina–Epoxy Composites

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6.1 Introduction

Potential of the ceramic-polymer composites is well realized since such a material system can effectively integrate compressive strength and fracture toughness of ceramic and polymer phases, respectively [2,5,142,143]. Among the different composite architectures, multilayered ceramic-polymer composite morphology is of particular interest. One approach to develop multilayered ceramic-polymer composite is the infiltration of open-cell sintered ceramic foam with polymer phase, followed by in situ polymerization. This methodology would require fabrication of ceramic foam with lamellar/dendritic (multilayered) morphology and directional porosity; however, the challenge is that the available techniques typically yield isotropic pore morphology with random orientations of pores. The ice-templating technique, on the other hand, produces macroporous ceramic with lamellar/dendritic morphology and directional porosity, in which parallel ceramic walls (oriented in the direction of temperature gradient applied during ice-templating) are connected in the transverse direction through ceramic bridges [2,5,17,24,25,28,29]. Due to low
pore tortuosity, ice-templated porous ceramic can be infiltrated with polymer solution to synthesize multilayered ceramic-polymer composite [11,144]. While there are studies on the 3-point bend response and fracture toughness measurements of ice-templated composites, their compressive deformation behavior remains relatively less addressed. Lightweight ceramic-polymer composites are ideal structural material candidates for mechanical load-bearing applications including dynamic (high-strain rate) loading conditions, where materials are subjected to compressive loading conditions.

For ice-templated ceramic-polymer composites, compressive response will not only depend on the composition but also on the loading direction. Therefore, for compression direction parallel to the layers, the ceramic phase will tend to dominate the macroscopic mechanical response and it is expected that compressive strength of the composite will be maximum along this orientation. Since, the changes in the microstructure of the ice-templated ceramic materials influence their compressive mechanical properties [29] such variations may also effect the compressive response of the resulting composites. Another important aspect is to address the compressive deformation behavior of ice-templated composites with respect to the compressive response of the individual components, i.e., ice-templated porous ceramic and polymer phase. To evaluate the performance of the composites in the dynamic loading environments, it is also crucial that compressive response of the composites is characterized both at quasistatic (low-strain rate) and dynamic (high-strain rate) regimes of strain rate.

In this study, to address the above aspects, ice-templated porous alumina (Al$_2$O$_3$) ceramics were developed from aqueous suspensions of same concentration (20 vol.% Al$_2$O$_3$), but freezing front velocity (FFV) during ice-templating process was systematically varied to alter the microstructure of the resulted porous ceramics. An ultrafine Al$_2$O$_3$ powder ($d_{50}$=300 nm) was
utilized based on our earlier studies which showed that finer ceramic powder particles produce ice-templated ceramics with dense lamella walls [24,25,28]. Next, porous ceramics were infiltrated with epoxy, which was followed by in situ polymerization to develop the composites. To understand the loading rate effects, uniaxial compressive response of the resulted composites were evaluated both in the quasistatic ($\sim 10^{-3} \text{s}^{-1}$) and dynamic ($\geq 10^{2} \text{s}^{-1}$) regimes of strain rate. In addition to the mechanical characterization of the ice-templated Al$_2$O$_3$-epoxy composites, compressive mechanical response of the individual components (i.e., ice-templated porous Al$_2$O$_3$ and epoxy) was investigated. The deformed ice-templated composites were characterized using a scanning electron microscope (SEM) to understand the possible origins of the observed failure response.

6.2 Experimental methodology

6.2.1 Synthesis of ice-templated porous alumina materials

Ultrafine Al$_2$O$_3$ powder ($d_{50}$=300 nm, APA-0.5, Sasol, Tuscan, AZ) was utilized to fabricate the ice-templated porous ceramics, and all the ceramics were processed from aqueous suspensions containing 20 vol.% Al$_2$O$_3$ particles. For each aqueous suspension, Al$_2$O$_3$ powder and an anionic dispersant (Darvan C, R.T. Vanderbilt Co., Norwalk, CT) were mixed first in deionized water in a Nalgene bottle, where Darvan C was taken in the proportion of 1 wt.% of Al$_2$O$_3$ powder. Next, zirconia (ZrO$_2$) spheres (~5 mm in diameter) were added to suspension (milling media was taken 4 times by mass of Al$_2$O$_3$ powder) and mixing of the suspension was conducted using a jar mill for 24 hours. After completion of the mixing cycle, an organic binder poly(2-ethyl-2-oxazoline) was added to the suspension (5 wt.% of Al$_2$O$_3$ powder) and the suspension was milled further for another hour. Afterward, the suspension was sieved to separate the ZrO$_2$ spheres and de-aired in low pressure for 30 min to remove any air bubbles entrapped in suspension.
Unidirectional ice-templating of Al₂O₃ suspensions was conducted employing a custom-made device. In this device, a Teflon tube is placed on a thin steel plate (referred to as “Cold-finger”), filled with an aqueous ceramic suspension, and the entire assembly is inserted inside a liquid nitrogen (N₂) Dewar and placed above the surface of liquid N₂. The temperature of Cold-finger reaches below 0°C, thus ice crystals nucleate at the bottom of suspension in contact with cold-finger and grow vertically under the influence of the temperature gradient. The thermally insulating Teflon tube ensures a unidirectional, vertical thermal gradient. By adjusting the distance between the Cold-finger and liquid N₂, the average unidirectional freezing-front velocity (FFV, i.e. the growth rate) of the ice crystals is controlled. In this study, ice-templating experiments were conducted at four different FFVs, where FFV was determined by dividing the height of a frozen sample with the time required for the completion of solidification. Frozen samples were of cylinder form (~18.5 mm in diameter and ~20 mm in height) and were freeze-dried at a low pressure (0.014 mbar) and temperature (-50°C) for 96 hours inside a freeze dryer (2.5L, Labconco, Kansas City, MI). Freeze dried samples were sintered at 1550°C for 4 hours in an air atmosphere inside a box furnace (KSL-1700X, MTI Corporation, Richmond, CA).

6.2.2 Characterization of ice-templated sintered porous Al₂O₃ materials: relative density, porosity, and microstructure

Dimension measurements of the sintered materials showed that each ice-templated porous ceramic was about 16.7 mm in diameter and 15.4 mm in height. From each sintered cylinder, a 6mm×6mm×3mm specimen was extracted. Mass and dimensions of the sintered porous ceramics were measured to estimate sintered density (ρ̂), whereas relative density (ρr) was determined as ρr = ρ̂/ρs, where ρs is the bulk density of α-Al₂O₃ (3.96 g/cm³). Total porosity was estimated using pt = (1 - ρr)×100. For microstructural characterization, a transverse plane (to the ice-growth
direction, referred to here as top plane) in each extracted specimen from a height of 8 mm from the bottom of sintered material was utilized and a Phenom ProX Tabletop SEM was employed. For each FFV regime, microstructural analyses were conducted for two randomly selected specimens.

6.2.3 Polymer infiltration of ice-templated sintered Al\textsubscript{2}O\textsubscript{3} materials and characterization

Extracted porous Al\textsubscript{2}O\textsubscript{3} specimens were infiltrated with a low-viscosity epoxy resin (EpoxiCure 2, Buehler) to develop composites. First, the epoxy resin was thoroughly mixed with a slow curing agent (EpoxiCure 2 Hardener, Buehler) and the mixture was subjected to a low pressure (0.1 MPa) inside a vacuum desiccator to any entrapped air bubbles. Next, an extracted Al\textsubscript{2}O\textsubscript{3} specimen was placed in the epoxy-curing agent mixture and infiltration was conducted under low pressure (0.1 MPa) for approximately 30 min. Next, the infiltrated specimen was removed and cured at room temperature for 24 hrs. These steps were followed to prepare each composite specimen. Here afterward, these infiltrated composites will be referred to as ice-templated Al\textsubscript{2}O\textsubscript{3}-epoxy composites or simply ice-templated composites. For comparison purpose, pure epoxy specimens were also prepared. After completion of the curing cycle, surfaces of each composite specimen were carefully ground and polished using 120, 300 and 600-grit silicon carbide papers. The density of each composite specimen ($\rho_{\text{comp}}$) was determined from the measurements of mass and dimensions. Relative density of each composite specimen ($\rho_{\text{r(comp)}}$) was determined as follows: measured relative density ($\rho_r$) of each extracted ceramic specimen (described in Section IV-B) was utilized to make the theoretical estimation of the composition (i.e., volume fractions of ceramic and polymer phases) of the corresponding composite sample (assuming 100% infiltration). For example, for a porous Al\textsubscript{2}O\textsubscript{3} specimen of $\rho_r$ of 0.3, theoretically estimated volume fractions of ceramic and polymer phases will be 0.3 and 0.7, respectively, for
6.2.4 Measurements of uniaxial compressive response

Uniaxial compressive response of ice-templated composites was characterized both at low- (\(\sim 10^{-3}/s\)) and high-strain rates (\(\geq 10^2/s\)). For each specimen, 6mm×6mm cross-section was the loading surface (i.e., compressed parallel to the ice-growth direction). A mechanical testing machine (MTS, ALLIANCE RF/300) was utilized for quasi-static compression experiments, using a displacement rate of 0.5 mm/min. On the other hand, a split Hopkinson pressure bar (SHPB) set up was employed for high-strain rate experiments. The SHPB set up consists of a solid striker bar of length 152.4 mm, a solid incident bar of length 1219.4 mm, and a solid transmission bar of length 914.4 mm; all the bars have a common diameter of 19.05 mm. All the solid bars are made out of high-strength maraging steel. Upon impact by the striker bar, a compressive stress pulse is produced in the incident bar, travels through the bar and loads the sample in compression. A part of the pulse is transmitted through the specimen to the transmission bar while the rest is reflected back to the incident bar. These stress pulses were utilized to determine the stress-strain response of the composite specimens [145]. For each SHPB experiment, a copper (Cu) pulse shaper was placed at the striker bar-incident bar interface to increase the rise time of the loading pulse and generate a triangular waveform. Stress pulses were measured through the strain gages (mounted in the middle of the incident and transmission bars) using a signal conditioning amplifier (2310B, Vishay) and a high-speed digitizer (NI PCI-5105, National Instrument). Stress in a specimen was estimated as [145]
\[ \sigma(t) = E \varepsilon_T(t) \frac{A_T}{A_S}. \quad (1) \]

In the above equation, \( E \) corresponds to the Young’s modulus of the bar material, \( \varepsilon_T(t) \) is the time-resolved axial strain in the transmission bar, and \( A_T \) and \( A_S \) are the cross-sectional areas of the transmission bar and sample, respectively. Similarly, strain rate in a specimen was estimated as [145]

\[ \dot{\varepsilon}(t) = -\frac{2c_0}{l_s} \varepsilon_R(t), \quad (2) \]

where \( c_0 \) is the wave velocity of the bar material, \( l_s \) is the original length of the specimen, \( \varepsilon_R(t) \) is the time-resolved axial strain of the reflected pulse in the incident bar. Strain in a specimen was calculated as [145]

\[ \varepsilon(t) = \int_0^t \dot{\varepsilon}_R(t). \quad (3) \]

For the purpose of comparison, the uniaxial compressive response of some of the porous Al\(_2\)O\(_3\) materials and pure epoxy specimens were also measured. For both porous ceramic and epoxy, specimens of 6mm×6mm×3mm dimensions were utilized (6mm×6mm cross-section being the loading direction). Since the porous ceramics and epoxy have low strength and modulus, a modified SHPB set up was employed to measure the compressive response. This modified set up is made of high-strength aluminum (Al) alloy, and consists of a solid striker bar of length 330.2 mm, a solid incident bar of length 1524 mm, and a solid transmission bar of length 914.4 mm; all the solid bars have a common diameter of 12.7 mm.

6.3 Results and discussion
6.3.1 Microstructural characteristics of ice-templated sintered alumina materials

Representative microstructures of the ice-templated porous Al₂O₃ materials, which were processed at four different FFVs, are shown in Figures 67a-d. Characteristic microstructural differences are observed in terms of the lamella wall thickness (t) and lamella wall spacing (i.e., wavelength, \( \lambda \)), where both the parameters decreased with increasing FFV. It can also be observed that there is a decrease in the pore size (pore major axis, \( a \), and minor axis, \( b \)) as well with the increasing FFV. Figures 67e and 67f show higher magnification SEM micrographs of ice-templated sintered Al₂O₃ materials processed at 20.2 \( \mu \)m/s and 27.8 \( \mu \)m/s, respectively, which reveal the significant decrease of \( t \) and \( \lambda \), and pore size with increasing FFV. Average values of the microstructural parameters such as \( a \), \( b \), pore area \( (A_p=\pi/4 \times a \times b) \), and pore aspect ratio \( (\chi_p=a/b) \) are provided in Table 5.
**Figure 59:** Representative SEM micrographs of ice-templated sintered porous Al₂O₃ materials which were processed at (a) 16.6 μm/s, (b) 20.2 μm/s, (c) 27.8 μm/s, and (d) 33.5 μm/s FFV, respectively. With the increase in FFV the macropores retain elliptical pore morphology. However, significant decrease in pore major axis \(a\), pore minor axis \(b\), lamellae spacing \(\lambda\) and, lamellae thickness \(t\) occurred with the increasing FFV, which can also be seen in 1(e) and 1(f) (ice-growth direction below and above the page). High magnification SEM micrograph observed from (g) cross-section of porous Al₂O₃ (ice-growth direction below and above the page), shows long slender dense ceramic lamella walls and (h) revealing the homogeneous dense polycrystalline microstructure in the lamella wall (ice-growth parallel to the page).
Table 5: Variation of pore characteristics in ice-templated porous Al$_2$O$_3$ materials as a function of FFV: major axis ($a$), minor axis ($b$), pore area ($A_p$), and aspect ratio ($\chi_p$).

<table>
<thead>
<tr>
<th>FFV ($\mu$m/s)</th>
<th>Pore characteristics</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average major axis ($a$) ($\mu$m)</td>
<td>Average minor axis ($b$) ($\mu$m)</td>
<td>Average area, $A_p$ ($\mu$m$^2$)</td>
<td>Aspect ratio ($\chi_p$)</td>
<td></td>
</tr>
<tr>
<td>16.9 ± 0.9</td>
<td>115.3 ± 8.6</td>
<td>14.4 ± 1.4</td>
<td>1310.6 ± 203.3</td>
<td>8.1 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>20.9 ± 1.0</td>
<td>124.2 ± 4.3</td>
<td>14.7 ± 1.8</td>
<td>1437.4 ± 226.5</td>
<td>8.5 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>26.8 ± 1.2</td>
<td>53.5 ± 11.1</td>
<td>6.4 ± 0.8</td>
<td>265.8 ± 44.1</td>
<td>8.7 ± 2.6</td>
<td></td>
</tr>
<tr>
<td>32.2 ± 1.4</td>
<td>76.6 ± 8.2</td>
<td>7.8 ± 0.6</td>
<td>471.8 ± 82.2</td>
<td>9.6 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Variation of density and porosity of ice-templated porous Al$_2$O$_3$ materials and ice-templated Al$_2$O$_3$-epoxy composites as a function of FFV.

<table>
<thead>
<tr>
<th>FFV ($\mu$m/s)</th>
<th>Ice-templated Al$_2$O$_3$</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho^*$ (g/cc)</td>
<td>$p_t$ (%)</td>
<td>$\rho_{comp}$ (g/cc)</td>
<td>$p_{t(comp)}$ (vol.%)</td>
<td></td>
</tr>
<tr>
<td>16.9 ± 0.9</td>
<td>1.12 ± 0.04</td>
<td>71.6 ± 1.0</td>
<td>1.95 ± 0.03</td>
<td>0.13 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>20.9 ± 1.0</td>
<td>1.31 ± 0.08</td>
<td>66.7 ± 2.1</td>
<td>2.01 ± 0.08</td>
<td>1.25 ± 2.2</td>
<td></td>
</tr>
<tr>
<td>26.8 ± 1.2</td>
<td>1.23 ± 0.1</td>
<td>68.9 ± 2.5</td>
<td>1.98 ± 0.11</td>
<td>2.65 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>32.2 ± 1.4</td>
<td>1.2 ± 0.06</td>
<td>69.5 ± 1.7</td>
<td>1.94 ± 0.05</td>
<td>2.13 ± 1.5</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Variation of density and porosity with FFV

The average values of density and porosity of ice-templated Al$_2$O$_3$ materials are listed in Table 6. It appears that initially average density ($\rho^*$) and porosity ($p_t$) of ice-templated Al$_2$O$_3$ materials increased and decreased, respectively, with increasing FFV, whereas a further increase of FFV seems to cause a slight decrease and increase of $\rho^*$ and $p_t$, respectively. Maximum and minimum $\rho^*$ values were observed to be 1.46 g/cc and 1.04 g/cc, respectively, whereas minimum and maximum $p_t$ values were observed to be 63 vol.% and 74 vol.%, respectively. Figure 67g shows a high magnification SEM micrograph of the cross-section of a lamella wall of the sintered Al$_2$O$_3$ processed at 32.9 $\mu$m/s, whereas Figure 67h shows the high magnification image of a lamella wall.
Both Figures 67g and 67h reveal the fine, polycrystalline microstructure of lamella walls and no visible porosity can be observed within the walls. Therefore, it can be assumed that in the sintered Al₂O₃ materials total pore volume corresponds to the macropores (i.e., macroporosity) present in between the dense lamella walls. Table 6 also shows the variation of average $\rho_{\text{comp}}$ and $p_{t(\text{comp})}$ of ice-templated Al₂O₃-epoxy composite specimens with average FFV. The maximum and minimum $\rho_{\text{comp}}$ values were observed to be 2.16 g/cc and 1.80 g/cc, respectively, whereas the minimum and maximum $p_{t(\text{comp})}$ values were observed to be 0 vol.% and 10.6 vol.%, respectively. Although, from microstructure analysis the locations of porosity were not apparent in the composites, it is speculated that porosity originated due to the incomplete infiltration of epoxy in ice-templated Al₂O₃.

6.3.3 Uniaxial compressive response at quasistatic regime of strain rate

Figure 68 shows the quasistatic (strain rate $\sim 10^3$ s⁻¹) stress-strain response of the ice-templated composites, up to 0.3 strain. In each figure, the average FFV value corresponds to the freezing condition for ice-templated Al₂O₃ materials, which were infiltrated to develop the ice-templated composites. All the composites exhibited a linear stress-strain response up to the peak stress (referred to as $\sigma_p$). Interestingly, at each FFV regime, a considerable difference in the overall compressive stress-strain curves is observed depending on the deformation response beyond peak stress. Mainly, two distinct features are noticeable in the measured compressive response. One set of composites exhibited a compressive response where stress dropped abruptly beyond peak stress (red curves), and we refer the failure type as catastrophic, i.e., a sudden loss of the compressive load-bearing capacity. Whereas, the other set of composites exhibited a compressive response where stress is observed to decrease gradually beyond peak stress (blue curves), which we refer to as progressive type failure. At each FFV regime, $\sigma_p$ values corresponding to catastrophic type
failure are observed to be significantly greater in comparison to that corresponding to progressive type failure.

**Figure 60:** Uniaxial quasistatic compressive stress-strain response of ice-templated Al₂O₃-epoxy composites processed at average FFV of (a) 17 ± 1.0 μm/s, (b) 20.6 ± 0.6 μm/s, (c) 26.9 ± 1.2 and, (d) 32.1 ± 1.3 μm/s. The numerical values shown in legend represent porosity (vol.%) in composite. The compressive stress-strain curves shown in blue color correspond to progressive type failure in composites, whereas the stress-strain curves shown in red color correspond to catastrophic type failure in composites.

Due to the significant scatter in the $\sigma_p$ values at each FFV regime, it is appropriate to group the stress-strain curves based on the type of compressive response (catastrophic failure vs. progressive failure) and for each group plot the average stiffness and strength values as a function of average FFV, which is presented in Figure 69. At each FFV regime, average stiffness corresponding to the ice-templated composites that exhibited catastrophic type failure is observed to be greater in
comparison to that of the composites that failed in a progressive manner, Figure 69a. Similar observations are also made for compressive strength (Figure 69b). For catastrophic failure average quasistatic $\sigma_p$ values are observed to be in the range of 398-575 MPa, whereas for progressive failure average quasistatic $\sigma_p$ values are observed to be in the range of 229-304 MPa. Although the measured compressive response does suggest some dependence on the FFV, more distinct is the differences of compressive response, i.e., catastrophic type failure vs. progressive type failure. At any FFV regime, ice-templated Al$_2$O$_3$-epoxy composites exhibited either a catastrophic type failure (brittle-like) with a relatively higher $\sigma_p$ or a progressive type failure (ductile-like) with a relatively lower $\sigma_p$. Figure 69c shows the variation of $\sigma_p$ as a function of the porosity of the porous Al$_2$O$_3$ materials, whereas Figure 69d shows the variation of $\sigma_p$ as a function of the porosity in the composites. In Figures 69c and 69d, a horizontal line is shown that approximately separates the region corresponding to catastrophic type failure from the region corresponding to progressive type failure, which suggests that failure type is independent of the porosity of both ice-templated porous ceramic and ice-templated composite.
**Figure 61:** Variations of quasistatic compressive mechanical properties of ice-templated Al$_2$O$_3$-epoxy composites as a function of FFV: (a) stiffness and (b) strength. Variations in quasistatic compressive strength of composites with porosity of (c) ice-templated porous Al$_2$O$_3$ and (d) ice-templated Al$_2$O$_3$-epoxy composite.

### 6.3.4 Influence of compressive mechanical properties of ice-templated porous Al$_2$O$_3$ and epoxy on the compressive response of ice-templated composite

It is expected that compressive mechanical properties of ice-templated porous Al$_2$O$_3$ and pure epoxy would have a governing influence on the compressive behavior of ice-templated composites. Recall that in this work, ice-templated porous Al$_2$O$_3$ materials were processed from aqueous suspensions of same solids loading (20 vol.%) but at different FFVs. To understand the effects of FFV on the compressive response of ice-templated porous materials, we processed another set of ice-templated porous Al$_2$O$_3$ materials within the same FFV range (Table 5) and Figure 70a shows the representative compressive stress-strain curves (up to 0.3 engineering strain) of the ice-templated Al$_2$O$_3$ materials. All the stress-strain curves feature a linear stress-strain part and a progressive deformation regime in which stress decreased gradually with the increasing strain. Compressive strength is observed to increase with the increasing FFV (Figure 70b); however, in the high FFV regime further increase of FFV only resulted in a slight increase of strength. We also compared the variation of density of ice-templated Al$_2$O$_3$ materials with FFV to that of the templated Al$_2$O$_3$ materials which were infiltrated to fabricate ice-templated composites. At comparable FFVs, density values of the porous Al$_2$O$_3$ materials used to fabricate composites are observed to be similar to those of the porous Al$_2$O$_3$ materials utilized to investigate the effects of the FFV on the compressive response. Therefore, we can state that at each FFV regime, the
compressive response of ice-templated Al₂O₃ materials (Figure 70a) represents the compressive response of the templated Al₂O₃ materials which were utilized to develop the composites. Figure 70c shows the uniaxial compressive response of pure epoxy phase (up to 0.3 engineering strain), which is characterized by a linear stress-strain part (elastic region), plastic strain-softening region, plateau region, and plastic strain-hardening region [146]. It can be seen that yield strength of epoxy is about 80 MPa, whereas deformation in the plateau and plastic strain-hardening regions progressed at stress levels well below 80 MPa. Thus, the compressive strength of ice-templated composites is observed to be markedly greater in comparison to the strength of the individual components, i.e., ice-templated porous Al₂O₃ (12.5 ± 4 MPa) and epoxy (80.3 ± 2 MPa). Therefore, there is an important role and structural advantage of ice-templated morphology in compressive load-bearing and markedly enhancing the compressive mechanical properties of the ice-templated composites relative to that of the individual components.

**Figure 62:** (a) Representative uniaxial compressive stress-strain curves (up to 0.3 engineering strain) of ice-templated porous Al₂O₃ materials. (b) Variations of compressive strength and density of ice-templated porous Al₂O₃ materials with FFV. (c) Uniaxial compressive response of epoxy phase (up to 0.3 engineering strain).
Ice-templated composites processed in this study can be treated as 1-3 diphasic solid [76] in which epoxy phase has connectivity only in a single dimension, where Al$_2$O$_3$ phase has connectivity in three-dimensions. In a two-phase composite material, conventionally matrix phase is considered to be the one that constitutes the major volume fraction of composite and has phase connectivity in more than one dimension, which also tends to have a governing influence on the macroscopic mechanical response of composite in comparison to the phase that constitutes minor volume fraction in the composite. In ice-templated composites, volume fractions of Al$_2$O$_3$ and epoxy phases are observed to be in between 0.26-0.37 and 0.63-0.74, respectively. While the epoxy phase constitutes the major volume fraction, the Al$_2$O$_3$ phase has the three-dimensional connectivity. Therefore, we attempted to provide some insights into the compressive response of ice-templated composite. For compression direction parallel to the ceramic and polymer layers, failure of the ceramic phase will tend to govern the strength of the composite ($\sigma_c$) and we can utilize equal-strain Voigt hypothesis (i.e., the rule of mixtures) to predict strength as [146]:

$$\sigma_c = \sigma_{epoxy} V_{epoxy} + \sigma_{Al_2O_3} V_{Al_2O_3}.$$  

(4)

$\sigma_{epoxy}$ and $\sigma_{Al_2O_3}$ correspond to the failure strength of epoxy and Al$_2$O$_3$ phases, respectively. Similarly, $V_{epoxy}$ and $V_{Al_2O_3}$ correspond to the volume fraction of epoxy and Al$_2$O$_3$ phases, respectively.

Figure 71 shows the comparison between the measured compressive strength of ice-templated composites and individual components and the calculated compressive strength ($\sigma_c$) of composites based on the rule of mixtures as a function of FFV. For the prediction of $\sigma_c$, we also estimated upper-bound (yellow shaded area) and lower-bound (gray shaded area) of strength based on the possible mode of failure in ceramic layers. The calculated upper-bound of strength is based on the assumption that thin ceramic lamella walls could sustain the applied compressive load and fail
axially without experiencing elastic instability (due to buckling) [76,147]. For this mode of failure, we considered uniaxial compressive strength of Al₂O₃ (2.5 GPa) for $\sigma_{\text{Al}_2\text{O}_3}$ [148]. On the other hand, under compression thin ceramic lamella walls can undergo bending, resulting in elastic instability within the walls and premature failure of composite. Therefore, to calculate the lower-bound of $\sigma_c$, we utilized 3-point bend strength of Al₂O₃ (510 MPa) for $\sigma_{\text{Al}_2\text{O}_3}$ [149]. For each bound of strength, we also obtained maximum and minimum of compressive strength ($\sigma_c$) based on the composition variation in the ice-templated Al₂O₃-epoxy composites. A dotted line is used which approximately separates the specimens that exhibited catastrophic type failure (above the dotted line) from those which exhibited progressive type failure (below the dotted line). It can be observed that the measured compressive strength values reside in between the calculated lower-bound and upper-bound of strength. Moreover, for the composite specimens which exhibited catastrophic type failure, strength values approach the upper-bound of calculated strength. Therefore, Figure 71 provides some meaningful insights into the compressive deformation behavior of ice-templated Al₂O₃-epoxy composite materials. Having the measured strength values below the upper-bound indicates that perhaps pure axial mode of failure is not dominant in ice-templated composites. It can be inferred that presence of epoxy layers in between the adjacent ceramic lamella walls provided a mechanical support to the walls which must have enhanced the resistance of the walls to elastic instability (i.e., buckling) and therefore the measured failure strength values of the composites are observed to be above the lower-bound of strength; however, under compression lamella walls eventually failed due to elastic instability and as a result upper-bound of strength was not achieved. It is possible that if the resistance of the walls to elastic instability increases significantly, compressive failure strength of ice-templated composites could approach the upper-
bound of strength, which might have occurred in the composite specimens which exhibited failure strength closer to the upper-bound of strength.

**Figure 63:** Comparison of measured compressive strength of ice-templated composites and its individual components with theoretically calculated compressive strength based on the rule of mixtures. (a) Compressive strength of ice-templated Al$_2$O$_3$ as a function of FFV; (b) Peak stress of pure epoxy under compression; (c) Based on rule of mixtures, compressive strength of ice-templated composites considering failure of ceramic walls by bending/buckling; (d) Compressive strength of ice-templated composites as function of FFV; (e) Based on rule of mixtures, compressive strength of ice-templated composites considering failure of ceramic walls under pure axial compression.

### 6.3.5 Uniaxial compressive response at dynamic regime of strain rate

Figure 72 shows uniaxial dynamic (strain rate 350-1800 s$^{-1}$) compressive stress-strain response (up to 0.1 strain) of ice-templated composites. In each figure the average FFV value corresponds
to the unidirectional freezing condition used for the ice-templated Al$_2$O$_3$ materials, which were infiltrated to develop the ice-templated composites. For the split Hopkinson pressure bar (SHPB) experimental conditions used in this study, we achieved compressive strain slightly above 0.1. Dynamic compressive response is observed to be similar to quasistatic compressive response. At each FFV regime, all the composite materials exhibited a linear stress-strain response up to peak stress ($\sigma_p$). Beyond peak stress, composites exhibited either catastrophic type failure (red curves) or progressive type failure (blue curves). Also, the dynamic $\sigma_p$ values corresponding to the catastrophic type failure are observed to be significantly greater in comparison to that corresponding to the progressive type failure.

**Figure 64**: Uniaxial dynamic (strain rate 350-1800 s$^{-1}$) compressive stress-strain response (up to 0.1 strain) of ice-templated composites processed at average FFV of (a) 16.9 ± 0.8 μm/s, (b) 20.8 ± 1.0 μm/s, (c) 26.6 ± 1.0 and, (d) 32.2 ± 1.4 μm/s. The numerical values shown in legend represent porosity (vol.%) in composite. The compressive stress-strain curves shown in blue color
correspond to progressive type failure in composites, whereas the stress-strain curves shown in red color correspond to catastrophic type failure in composites.

Similar to the quasistatic data, at each FFV regime, we also separated the dynamic $\sigma_p$ values into two groups, based on the type of failure, i.e., catastrophic vs. progressive. Figure 73a shows the variation of average dynamic $\sigma_p$ values as a function of average FFV corresponding to catastrophic and progressive failure. For the purpose of comparison, quasistatic $\sigma_p$ values are also included. At each FFV regime, dynamic $\sigma_p$ corresponding to catastrophic type failure is observed to be significantly greater in comparison to dynamic $\sigma_p$ corresponding to progressive type failure. Also, for each type of failure, dynamic $\sigma_p$ is observed to be considerably greater in comparison to quasistatic $\sigma_p$. For catastrophic type failure, average dynamic $\sigma_p$ values are observed to be in the range of 671-721 MPa, whereas average quasistatic $\sigma_p$ values are observed to be in the range of 398-575 MPa. For progressive type failure, average dynamic $\sigma_p$ values are observed to be in the range of 326-426 MPa, whereas average quasistatic $\sigma_p$ values are observed to be in the range of 229-304 MPa. Therefore, irrespective of the strain rate regime, ice-templated composites exhibited both catastrophic type and progressive type failure. And, irrespective of the type of failure, composites exhibited a pronounced enhancement of strength under dynamic loading in comparison to the quasistatic loading.
**Figure 65:** (a) Comparison of dynamic and quasistatic compressive strength of ice-templated composites as a function of FFV. For each type of loading condition, the data shown in blue color correspond to progressive type failure in composites, whereas the data shown in red color correspond to catastrophic type failure in composites. (b) Representative dynamic compressive response of ice-templated porous Al₂O₃, epoxy, and ice-templated Al₂O₃-epoxy composites (corresponding to both catastrophic and progressive type failure). (c) Quasistatic compressive stress-strain curves of ice-templated composites which exhibited progressive type failure. Also, included stress-strain response of epoxy phase.

Therefore, the present experimental work revealed that uniaxial compressive mechanical response of ice-templated composites is strain rate sensitive. It is known that uniaxial compressive mechanical response of Al₂O₃ ceramic and epoxy is strain rate sensitive [70,72,149,150]. Therefore, it is expected that the rate sensitivity of ice-templated composites could be related to the rate sensitivity of Al₂O₃ and epoxy phases as well as to the ice-templated morphology. Our recent work [76,151] revealed that for ice-templated Al₂O₃ materials processed from 20 vol.%
Al₂O₃ suspension (same composition used in this work), dynamic compressive strength was moderately higher relative to quasistatic compressive strength. On the other hand, for ice-templated Al₂O₃ ceramics with higher ceramic content, compressive strength was observed to be comparable across the quasistatic and dynamic regimes of strain rate [76]. Similar results have been reported for various other cellular solid materials including open-cell and closed-cell aluminum (Al) foams, Al alloy/silicon carbide (SiC) hollow sphere syntactic foams, cp-Al/cenosphere syntactic foams, and amorphous metal foam, in which maximum uniaxial compressive strength did not exhibit any measurable strain rate sensitivity [98,152–154]. One possible rationale is that while the compressive strength of Al₂O₃ is rate sensitive, in the porosity range of 54-70 vol.%, contribution of the Al₂O₃ phase to the strain rate sensitivity of the compressive response of ice-templated Al₂O₃ materials could be insignificant [76]. In cellular solids, rate sensitivity can also result from the local dynamic effects due to the rapid crushing of cell walls, which is referred to as micro-inertia effects [111,113,154–157]. These effects can become dominant during two stages of deformation, during the (i) collapse of cell walls at the onset of compressive fracture and (ii) during the progressive deformation in the stress plateau regime. As a result, under dynamic loading conditions, cellular solids can exhibit stress enhancement for failure initiation (peak stress) and/or failure propagation (plateau stress). In the dynamic loading regime, microstructural deformation mechanisms such as bending and buckling of struts and fracture of cell walls are affected by the micro-inertia effects [158]. Therefore, it is important to consider the probable role of the micro-inertia effects in relation to the dynamic response of both ice-templated porous ceramic and ice-templated ceramic-polymer composite.

Under compressive loading, elastic instability due to buckling can cause brittle fracture within the lamella walls of ice-templated ceramic materials [76,147]. Dynamic strength enhancement due
to micro-inertia effects can become significant when the asymmetric mode of deformation such as buckling is associated with the deformation process in cellular solids [158,159]. It is known that under dynamic loading, lateral inertia of cell walls can suppress the more compliant asymmetric mode of cell deformation and thereby material exhibits a dynamic stress enhancement before the asymmetric mode of deformation is triggered. As a result, micro-inertia effects can delay the initiation of elastic instability within the lamella walls of ice-templated ceramic and result in an increase of compressive strength (i.e., $\sigma_p$) relative to that under quasistatic loading conditions.

Figure 73b shows the representative high-strain rate uniaxial compressive response of ice-templated porous Al$_2$O$_3$, epoxy, and ice-templated Al$_2$O$_3$-epoxy composites (corresponding to both catastrophic type and progressive type failure). Dynamic compressive strength of ice-templated composite is observed to be markedly greater than the dynamic strength of both ice-templated porous Al$_2$O$_3$ and epoxy. A comparison of Figure 70 and Figure 73b shows that there is some increase of compressive strength for both porous Al$_2$O$_3$ and epoxy under dynamic loading relative to quasistatic loading. We suggest that under dynamic loading conditions, lamella walls of ice-templated Al$_2$O$_3$ exhibit greater resistance to buckling relative to quasistatic loading and thereby are able to carry a higher amount of compressive load. Moreover, strength enhancement of epoxy in the high-strain rate regime could provide a greater mechanical support to the lamella walls relative to that under quasistatic loading. While the dynamic strength enhancement of the individual phases (i.e., ice-templated porous Al$_2$O$_3$ and epoxy) could attribute to the dynamic compressive response, it is the ice-templated morphology which provides a greater structural advantage for compressive load-bearing in the high-strain rate regime relative to the quasistatic strain rate regime. As a result, in spite of the marginal strength enhancement in the individual
components (porous Al₂O₃ and epoxy), the dynamic compressive strength of ice-templated composite was markedly enhanced in comparison to quasistatic compressive strength.

6.3.6 On the origin of catastrophic and progressive failure in ice-templated composites

Irrespective of the strain rate regime, ice-templated ceramic-polymer composites exhibited both catastrophic and progressive types of failure. Our results did not suggest any direct correlation between the FFV or porosity and the type of failure. As discussed earlier, for compression direction parallel to the ceramic and polymer layers, failure within the ceramic phase will tend to govern the strength of the composite. Therefore, irrespective of the type of failure, it is expected that brittle fracture in ice-templated ceramic structure will trigger macroscopic failure in the composite. While brittle fracture in ice-templated ceramic can set the limit for maximum compressive strength in composite, it may not necessarily directly attribute to the contrasting failure behavior which we observed in the compressive response of the ice-templated composites.
**Figure 66:** SEM images of ice-templated composite specimens which exhibited catastrophic type failure (a-c) and progressive type failure (d-f). All the images were taken from planes perpendicular to the compressive loading direction (ice-growth direction below and above the page).

The catastrophic type failure in ice-templated composite resembles to the brittle mode of failure, whereas the progressive type failure can be treated as the ductile mode of failure. For the catastrophic type of failure, during compression elastic strain energy stored in composite corresponding to peak stress might have been high enough to result in complete loss of compressive load-bearing capacity. Indeed, the composite specimens that exhibited catastrophic failure were completely shattered upon reaching the maximum stress. On the other hand,
composite specimens which exhibited progressive type failure were partially intact beyond peak stress and thereby able to maintain the compressive load-bearing capacity to some extent. Figure 73c shows the quasistatic compressive stress-strain curves of the ice-templated composite specimens which exhibited progressive type failure. Included also is the stress-strain response of epoxy phase. It can be observed that during progressive failure stage, deformation in composite proceeded at a stress level that is considerably greater relative to the plateau stress in epoxy. We suggest that in ice-templated composites progressive deformation stage proceeds by the plastic deformation of epoxy; however, the presence of ice-templated ceramic architecture enhanced the resistance of epoxy to plastic deformation and thereby composites exhibited greater plateau stress relative to epoxy.

Based on the above discussion, it can be argued that the observed progressive type of deformation resulted from a premature, early stage failure in ice-templated composites in contrast to composites which exhibited catastrophic type failure. At the initiation of failure, stored strain energy might have been insufficient to cause abrupt failure in the composite; however, the stress level was high enough to initiate plastic deformation in the composite. Since the probability of failure in ice-templated composites either by catastrophic or progressive mode was observed to be random, it is possible that mode of failure was governed by the characteristic of damage initiation and propagation. To shed some light into this, we analyzed the fragments of the ice-templated composites corresponding to both catastrophic type and progressive type failure.

Figure 74 shows SEM images of the composite specimens that exhibited catastrophic type failure (a-c) and progressive type failure (d-f). All the images were taken from planes perpendicular to the compressive loading direction (also the ice crystal growth direction). Figure 74a shows a low-magnification SEM image of the characteristic of long crack propagation in the
ice-templated composite which exhibited catastrophic type failure, whereas a high-magnification SEM image (Figure 74b) reveals that such cracks propagated along the epoxy-Al₂O₃ interface. Microstructure analysis further revealed long crack propagation perpendicular to the layers as seen in Figure 74c. Similar characteristics of crack propagation were as well observed in the composites that exhibited progressive type failure (Figure 74d); however, the microstructural analysis also revealed severely cracked regions (which appear to be epoxy rich) in these composites as indicated in Figures 74e-f and such damaged regions were readily observable during microscopy. It is to note that such damaged epoxy rich regions were not present in the undeformed composites. Based on these observations we made the following arguments to rationalize the failure of composites in catastrophic mode and progressive mode.

Irrespective of the type of failure, long cracks along the ceramic-polymer interface and perpendicular to the layers were observed within the fragments of the composite specimens. We suggest that such long cracks ultimately resulted in the fragmentation of the composite specimens and therefore formation of long cracks can be considered as the primary mechanism of axial splitting under compression in ice-templated composites. Whereas, cracking within the epoxy rich regions limited the load-bearing capacity and initiated early stage failure (i.e., lower peak stress) in the composites that exhibited progressive type failure response. As the progressive deformation continued, eventually macroscopic crack propagation occurred resulting in the fragmentation of the specimens. In the absence of cracking within the epoxy rich regions, the composites specimens were able to sustain a greater level of compressive load and as a result catastrophic type of failure occurred at a peak stress level that was significantly greater in comparison to that of the composites which exhibited progressive type failure. In ice-templated ceramics, all the lamella walls are not perfectly oriented with respect to the ice crystal growth direction [160,161], which could also
attribute to the observed modes of failure in ice-templated composites. Perfectly aligned ceramic walls with respect to the loading direction would exhibit resistance to shear, whereas walls misaligned with respect to the loading orientation can undergo local shear failure and cause early stage failure, i.e., lowering peak stress. The composite specimens exhibited both types of failure almost in equal probability. Therefore, it is possible that in the specimens that exhibited progressive type failure, early stage damage initiation might have triggered by the misalignment of the walls with respect to the loading direction.

6.4 Conclusions

This work investigated the compressive mechanical response of ice-templated alumina-epoxy composite materials and studied the effects of strain rate. Ice-templated porous Al₂O₃ materials were processed from aqueous suspensions of same ceramic content (20 vol.%) but over a range of FFV. Microstructural analysis revealed variations of lamella wall thickness and spacing as well as pore characteristics with FFV; however, the overall morphology was observed to be primarily lamellar. Porous Al₂O₃ materials were infiltrated with epoxy to develop composites.

While the compressive response measurements of composites suggested some dependence on FFV, more distinct was the differences of stress-strain curves depending on the compressive response beyond peak stress. Ice-templated composites exhibited either a catastrophic type failure (brittle-like) with a relatively higher peak stress or a progressive type failure (ductile-like) with a relatively lower peak stress. It was also observed that the failure type was independent of the porosity of both porous ceramic and composite. The compressive mechanical response of the individual components (i.e., ice-templated porous Al₂O₃ and epoxy) were also studied, which showed that compressive strength of ice-templated composites was markedly greater in comparison to the strength of the individual components. The experimental results were analyzed
using the rule of mixtures, which suggested that perhaps pure axial mode of failure was not dominant in ice-templated composites, and the presence of epoxy layers in between the adjacent ceramic lamella walls provided a mechanical support to the walls which enhanced the resistance of the walls to elastic instability (i.e., buckling) and therefore the measured failure strength values of composites were observed to be above the predicted lower-bound of strength.

Characteristics of the dynamic compressive response of ice-templated composites were similar to that observed in the quasistatic regime of strain rate; however, for both types of failure, the compressive strength was significantly greater relative to the quasistatic counterpart. Under dynamic loading, lamella walls of ice-templated Al₂O₃ could have exhibited greater resistance to buckling relative to quasistatic loading and thereby were able to carry a higher amount of compressive load. Moreover, strength enhancement of epoxy in the high-strain rate regime provided a greater mechanical support to the lamella walls relative to that under the quasistatic loading conditions. Overall, ice-templated morphology could have provided a greater structural support for compressive load-bearing in the high-strain rate regime relative to the quasistatic strain rate regime. Finally, some insight was provided into the origin of catastrophic and progressive types of failure in ice-templated composites through the microstructural analysis of the deformed composite specimens.

Acknowledgment

CHAPTER 7

ASSESSING THE ROLE OF LOADING DIRECTION ON THE UNIAXIAL COMPRESSIVE RESPONSE OF MULTILAYERED ICE-TEMPLATED ALUMINA-EPOXY COMPOSITES

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7.1 Introduction

Composites with alternate layers of ceramic and polymer phases are of profound interest in the pursuit of damage-tolerant materials [2,5,142]. The role of the ceramic phase is to withstand high mechanical stresses and resist failure. Whereas, the polymer phase attributes toughness and enables energy dissipation. A structural gradient in multilayered architecture can enable the design of functionally graded materials (FGMs), a feature that we witness in several natural materials, which allows them to exhibit gradient in mechanical properties [4,6]. Liu et al. [11] recently discussed that gradient in structural orientation in living organisms, such as nacreous shell, pangolin scale, crayfish mandible, tooth dentin, and tooth enamel, is the source of their enhanced surface protection to penetration and deformation under contact loading. Due to the presence of structural gradient, under mechanical loading, the outermost regions in these materials respond differently in comparison to the interior regions, enabling gradient in mechanical properties [12,13,16,101]. The concept of gradient structural orientation can enable graded mechanical
properties in multilayered composites, further enhancing the usability of this class of materials in engineering applications. While enticing, to realize the potential of such architecture in materials design, a pivotal step is first to understand the mechanical behavior of multilayered ceramic-polymer materials that remains premature. A pressing need is to characterize the loading orientation dependence of mechanical response under compressive loading [87]. This investigation is not on the development of multilayered ceramic-polymer composites with a structural gradient. However, it takes a pivotal step to characterize the role of loading direction relative to layer orientation on the compressive response, using ice-templated alumina-epoxy composite as a model system.

In the ice-templating technique [17,22,51,137], an aqueous ceramic suspension is unidirectionally solidified. Next, freeze-drying and sintering result in directionally porous ceramic materials. Ice-templated ceramics contain ceramic lamella walls, directional pores present between the walls, and lamellar bridges that connect the walls [24,25,28,29,55,93]. All the lamella walls are oriented along the growth direction of ice crystals that develop during the templating step—infiltiration with polymer results in multilayered ceramic-polymer composites [5,43,50]. We can characterize the resultant composites under uniaxial compression for different loading directions relative to the growth direction of ice crystals. There are several advantages of using ice-templated composites as a model system, such as the ease of changing the composition (i.e., ceramic to polymer ratio), layer thickness, and layer connectivity [140,144]. For compression direction parallel (θ = 0°, iso-strain condition) and perpendicular (θ = 90°, iso-stress condition) to the growth direction of ice crystals, ceramic and polymer phases, respectively, will tend to govern the strength of the composite. Thus, for different θ values, characterization of the compressive response of ice-
templated composites can provide insights into the mechanical behavior of multilayered composites, and valuable guidance to design materials with graded mechanical properties.

7.2 Experimental

7.2.1 Fabrication of ice-templated ceramic-polymer composites

Composites were developed from alumina (Al$_2$O$_3$) ceramic and a low-viscosity epoxy resin (EpoxiCure 2, Buehler). Macroporous Al$_2$O$_3$ materials were synthesized using the ice-templating technique, and sintered porous ceramics were infiltrated with epoxy. The resultant Al$_2$O$_3$-epoxy composite materials are simply referred to here as ice-templated composites. A custom-made device was utilized to synthesize ice-templated ceramics from aqueous suspensions of Al$_2$O$_3$ particles. Ultrafine Al$_2$O$_3$ powder ($d_{50} = 300$ nm, APA-0.5, Sasol, Tuscan, AZ) was utilized, and the following procedure was utilized to prepare aqueous ceramic suspensions. The required amount of deionized water and ammonium polymethacrylate anionic dispersant (Darvan C, R.T. Vanderbilt Co., Norwalk, CT, 1 wt.% of Al$_2$O$_3$ powder) were taken into a Nalgene bottle; then, a measured amount of Al$_2$O$_3$ powder was added to the bottle. Next, zirconia (ZrO$_2$) spheres were added to the aqueous suspension and milled for 24 hrs. An organic binder solution of poly(2-ethyl-2-oxazoline) was next added to the suspension (5 wt.% of Al$_2$O$_3$ powder), and the suspension was further mixed for an hour. Next, the ZrO$_2$ spheres were separated from the suspension, and the suspension was de-aired for 30 minutes.

Ice-templated Al$_2$O$_3$ materials were synthesized from aqueous suspensions of two compositions: 20 vol.% Al$_2$O$_3$ content and 30 vol.%. The composition variation was done to vary ceramic and polymer contents in the composites. A custom-made device was employed to freeze the aqueous suspensions unidirectionally, the details of the ice-templating process can be found
elsewhere [19]. A hollow Teflon mold is filled with aqueous ceramic suspension and the mold is placed on a thin steel plate (“Cold-finger”). The whole assembly is inserted into a liquid nitrogen (N\textsubscript{2}) Dewar and placed above the liquid N\textsubscript{2} surface. As the temperature of the Cold-finger falls below 0 °C, ice crystals nucleate on the Cold-finger and the crystals grow upward under the influence of applied temperature gradient. The freezing-front velocity (FFV) is controlled by adjusting the distance between the Cold-finger and liquid N\textsubscript{2} surface. After ice-templating, solidified samples were obtained, which contained alternate layers of ceramic and ice, both layers oriented in the direction of the applied unidirectional temperature gradient. An average FFV was determined by dividing the height of frozen sample to time required for completion of solidification. Materials from 20 vol.% Al\textsubscript{2}O\textsubscript{3} suspensions were processed at relatively high FFV (28.4 ± 1.9 µm/s), whereas materials from 30 vol.% Al\textsubscript{2}O\textsubscript{3} suspensions were processed at relatively high FFV (28 ± 1.4 µm/s) and low FFV (14.1 ± 0.6 µm/s). The frozen samples were of cylinder form (~18.5 mm in diameter and ~20 mm in height) and freeze-dried at low pressure (0.014 mbar) and temperature (-50°C) for 96 hours inside a freeze dryer (2.5L, Labconco, Kansas City, MI). Freeze-dried samples were sintered at 1550°C for 4 hours in an air atmosphere inside a box furnace (KSL-1700X, MTI Corporation, Richmond, CA).

The sintered Al\textsubscript{2}O\textsubscript{3} materials were approximately 17 mm in diameter and 15.6 mm in height. From each sintered cylinder, two 6 mm x 6 mm x 3 mm specimens were extracted. As shown schematically in Figure 75, porous ceramic specimens were extracted at different angles, θ, relative to the growth direction of ice crystals. Thus, θ represents the angle between the compression direction and growth direction of ice crystals. Note that lamella walls are oriented along the growth direction of ice crystals. Therefore, θ also represents the angle between loading direction and wall orientation. While Figure 75 shows that specimens were extracted for θ at 0,
45, and 90°, specimens were extracted at 5, 10, 15, and 20° as well for each set of composites. Figure 75 also illustrates the locations from where the specimens were extracted. The following steps were performed for the polymer infiltration. First, an epoxy resin was mixed with a slow curing agent (EpoxiCure 2 Hardener, Buehler), and the mixture was subjected to low pressure (0.1 MPa) inside a vacuum desiccator to remove entrapped air bubbles. Next, a sintered porous Al₂O₃ specimen was placed in the epoxy-curing agent mixture, and infiltration was performed at low pressure (0.1 MPa) for 30 minutes. Next, the infiltrated specimen was removed and cured at room temperature for 24 hrs. These steps were followed to prepare each composite specimen. For comparison, pure epoxy specimens were also prepared.

**Figure 67:** Schematics showing that porous ceramics were extracted at different angles, θ, relative to the growth direction of ice-crystals. θ also represents the angle between loading direction and ceramic wall orientation. Also, shows the locations from where specimens were extracted.
7.2.2 Characterization of ice-templated ceramics and composites: relative density, porosity, microstructure, and uniaxial compressive response

Mass and dimensions of the extracted specimens were measured for the estimation of sintered density ($\rho^*$) of porous ceramic. Relative density ($\rho_r$) was calculated as $\rho_r = \rho^*/\rho_s$, where $\rho_s$ is the bulk density of dense $\alpha$-Al$_2$O$_3$ (3.96 g/cm$^3$). Total porosity was estimated using $p_t = (1 - \rho_r) \times 100$. Post infiltration, surfaces of each composite specimen were carefully ground and polished using 120, 300, and 600-grit silicon carbide papers. The density of each composite specimen ($\rho_{comp}$) was determined from the measurements of mass and dimensions. The relative density of each composite specimen ($\rho_r(comp)$) was determined as follows. The calculated $\rho_r$ from each extracted ceramic specimen was utilized to make the theoretical estimation for the composition (i.e., volume fractions of ceramic and polymer phases) of the corresponding composite sample (assuming 100% infiltration). For example, a porous Al$_2$O$_3$ specimen with $\rho_r$ of 0.3, theoretically estimated volume fractions of ceramic and polymer phases will be 0.3 and 0.7, respectively, for the corresponding infiltrated composite (assuming complete infiltration). Next, the theoretical density of the composite ($\rho_{comp(cal)}$) was calculated based on the rule of mixtures. Finally, the relative density of composite was estimated using $\rho_r(comp) = \rho_{comp}/\rho_{comp(cal)}$, and total porosity of the composite was calculated as $p_{t(comp)} = (1 - \rho_{r(comp)}) \times 100$. For microstructure characterization, a Phenom desktop SEM was employed.

Uniaxial compressive response of ice-templated composites was characterized at low-strain rates ($\sim 10^{-3}$/s), and a mechanical testing machine (MTS, ALLIANCE RF/300) was utilized, using a displacement rate of 0.5 mm/min. For each composition and orientation, compression tests of at least three specimens were imaged using a FASTCAM SA4, Photron camera to capture damage evolution in the specimens. Imaging speed of 60 frames per second was used with a
resolution of $1024 \times 512$ pixels. For better visualization, speckle pattern was applied on specimen surfaces. Due to the low strength, porous specimens and pure epoxy were characterized at similar conditions using Tinius Olsen (model 10ST) mechanical testing machine equipped with a 10 kN load cell. For any given composition, FFV, and orientation, at least 15 specimens were tested for porous ceramics and composites.

7.3 Results

7.3.1 Porosity and microstructure

Figure 76 shows the variation of density ($\rho_{\text{comp}}$) and porosity ($p_{t(\text{comp})}$) of composite specimens with the porosity ($p_t$) of the specimens extracted from the ice-templated sintered porous Al$_2$O$_3$ materials. The average values are also provided in Table 7. The porosity of ice-templated sintered ceramics developed from suspensions containing 20 vol.% Al$_2$O$_3$ is 69.4 ± 0.9 vol.%, and the density of the corresponding composite specimens is 1.98 ± 0.1 g/cm$^3$. Similarly, the porosity of ice-templated sintered ceramics developed from suspensions containing 30 vol.% Al$_2$O$_3$ at low FFV is 59.3 ± 1.6 vol.%, and the density of the corresponding composite specimens is 2.34 ± 0.1 g/cm$^3$. Whereas, the porosity of ice-templated sintered ceramics developed from 30 vol.% suspensions at high FFV is 52.9 ± 2.4 vol.%, and the density of the corresponding composite specimens is 2.42 ± 0.1 g/cm$^3$. Maximum porosity in the composite specimens is about 3 vol.%, and the data thus suggest that almost complete infiltration was achieved for most of the specimens.
Figure 68: Variation of density, $\rho_{\text{comp}}$, and porosity, $p_{t(\text{comp})}$, of ice-templated Al$_2$O$_3$-epoxy composites with porosity, $p_t$, of ice-templated ceramics.

Table 7: Variation of density ($\rho_{\text{comp}}$) and porosity ($p_{t(\text{comp})}$) of ice-templated Al$_2$O$_3$-epoxy composites with porosity ($p_t$) of ice-templated sintered Al$_2$O$_3$ materials prior infiltration. The error represents the standard deviation of minimum fifteen independent samples.

<table>
<thead>
<tr>
<th>Composite ID</th>
<th>$p_t$ (vol.%$)$</th>
<th>$\rho_{\text{comp}}$ (g/cm$^3$)</th>
<th>$p_{t(\text{comp})}$ (vol.%$)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20C-H</td>
<td>69.4 ± 0.9</td>
<td>1.98 ± 0.0</td>
<td>1.5 ± 1.1</td>
</tr>
<tr>
<td>30C-L</td>
<td>59.3 ± 1.6</td>
<td>2.34 ± 0.10</td>
<td>0.76 ± 0.3</td>
</tr>
<tr>
<td>30C-H</td>
<td>52.9 ± 2.4</td>
<td>2.42 ± 0.1</td>
<td>2.6 ± 1.7</td>
</tr>
</tbody>
</table>

SEM images of ice-templated sintered Al$_2$O$_3$ materials are shown in Figure 77. Morphology of the materials fabricated from 20 vol.% Al$_2$O$_3$ suspensions are lamellar, which is characterized by large elongated pores with insignificant lamellar bridges. Due to the lamellar
morphology in the materials processed at high FFV, materials from 20 vol.% Al₂O₃ suspensions were not fabricated at low FFV. These porous materials are referred to as 20P-H, and the corresponding composites are referred to as 20C-H. Whereas, for 30 vol.% Al₂O₃ suspensions, for high and low FFV processing conditions, material morphology is observed to be dendritic and lamellar, respectively. The lamella walls are observed to be thicker compared to the materials developed from 20 vol.% suspensions. At high FFV, significant lamellar bridges developed, and both wall thickness and pore size are observed to be smaller compared to the low FFV materials. For 30 vol.%, porous materials are referred to as 30P-H and 30P-L for high FFV and low FFV, respectively, and the corresponding composites are referred to as 30C-H and 30C-L, respectively. Table 8 lists the average values and standard deviations of lamella wall thickness ($t$), pore major axis ($a$), pore minor axis ($b$), pore aspect ratio ($\chi$), and pore area ($A_p$) of 20P-H, 30P-L, and 30P-H ceramics. The mass transport phenomenon during the densification of powder particles can be enhanced by a decrease in radius of curvature of pores [25,26]. Since pore size in 30P-H ceramics is smaller than in 30P-L ceramics, pores in the former materials are of smaller radius of curvature than in the later ceramics. As a result, ice-templated ceramics fabricated from 30 vol.% Al₂O₃ suspensions at high FFV exhibited lower porosity compared to the materials fabricated from the same suspensions at low FFV.
Figure 69: Representative SEM images of ice-templated sintered porous Al₂O₃ materials. (a) Material developed from 20 vol.% Al₂O₃ suspensions at relatively high FFV (28.4 ± 1.9 µm/s), 20P-H. Porous materials developed from 30 vol.% Al₂O₃ suspensions at relatively (b) low FFV (14.1 ± 0.6 µm/s), 30P-L, and (c) high FFV (28 ± 1.4 µm/s), 30P-H.

Table 8: Microstructural features of ice-templated sintered Al₂O₃ materials. The error represents the standard deviation of minimum 1000 measurements from 3 independent samples.

<table>
<thead>
<tr>
<th>Composite ID</th>
<th>Wall thickness ( t ) (µm)</th>
<th>Pore major axis ( a ) (µm)</th>
<th>Pore minor axis ( b ) (µm)</th>
<th>Pore aspect ratio</th>
<th>Pore area ( A_p ) (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20P-H</td>
<td>8.5 ± 1.0</td>
<td>34.5 ± 4.6</td>
<td>4.5 ± 0.7</td>
<td>7.7</td>
<td>124.3 ± 32.1</td>
</tr>
<tr>
<td>30P-L</td>
<td>16.4 ± 0.9</td>
<td>43.1 ± 8.2</td>
<td>9.0 ± 0.9</td>
<td>4.8</td>
<td>310.2 ± 87.2</td>
</tr>
<tr>
<td>30P-H</td>
<td>10.5 ± 0.5</td>
<td>20.2 ± 1.1</td>
<td>4.9 ± 0.1</td>
<td>4.1</td>
<td>77.6 ± 5.9</td>
</tr>
</tbody>
</table>

7.3.2 Compressive response of ice-templated composites

Figures 78a-g show the influence of \( \theta \) on the uniaxial compressive response of 20C-H composites. Figure 78h shows the compressive response of pure epoxy. Similarly, Figures 79a-c show uniaxial compressive stress-strain curves of 30C-H composites for \( \theta \) at 0, 45, and 90°, whereas Figures 79d-f show stress-strain curves of 30C-L composites for \( \theta \) at 0, 45, and 90°.
Legends in the figures represent porosity in the composite specimens. Although at each $\theta$ at least 15 specimens were tested, only a few stress-strain curves are shown, representing the material behavior. The uniaxial compressive response of pure epoxy is characterized by a linear stress-strain part (elastic region), plastic strain-softening region, and plateau region [146]. The measured yield strength of epoxy is in the range of 70-90 MPa, whereas the deformation in the plateau region progressed at a stress level below 90 MPa.

**Figure 70**: (a)-(g) Variation of uniaxial compressive response of ice-templated 20C-H composites with $\theta$. Legends represent porosity in the composites. (h) Uniaxial compressive response of pure epoxy.
At $\theta = 0^\circ$, 20C-H composites exhibited significant variability in maximum compressive strength (peak stress, $\sigma_p$). Specimens that exhibited high failure strength also experienced an abrupt drop of stress beyond peak stress, which we refer to as catastrophic-type (brittle-like) failure. Whereas, specimens with strength on the lower end of the strength spectrum exhibited a gradual decrease in strength beyond peak stress, behavior that we refer to as progressive-type (ductile-like) failure. Progressive deformation is accompanied by plastic deformation in epoxy and continuous fracture of ceramic walls. The current observation is consistent with our recent work on ice-templated Al$_2$O$_3$-epoxy composites performed for a similar composition for compression direction parallel to the growth direction of ice crystals [42]. However, the focus of the previous study was on the influence of strain rate on the compressive response for loading direction parallel to the growth direction of ice crystals. At $\theta = 5^\circ$, materials exhibited behavior comparable to that captured for $\theta = 0^\circ$. With a further increase in $\theta$ to $10^\circ$, composite strength decreased significantly, but the materials exhibited both types of failure. At $\theta = 15^\circ$, strength decreased drastically; however, all the specimens exhibited progressive-type failure. In the range of $15^\circ$–$45^\circ$, strength decrease is less significant compared to the $0^\circ$–$15^\circ$ range, and the composites exhibited progressive-type failure. By $\theta = 45^\circ$, the compressive response of composites became comparable to that measured for $\theta = 90^\circ$ in terms of signature of stress-strain curves, although strength decreased significantly between $\theta = 45^\circ$ and $\theta = 90^\circ$. Because of the similarity in failure response, we did not characterize uniaxial compressive response for $45^\circ < \theta < 90^\circ$. At $\theta = 90^\circ$, the compressive response of the composites has a high resemblance to that of epoxy with maximum strength only marginally higher compared to that of epoxy. For 30C-L and 30C-H composites, tested for $\theta$ of $0^\circ$, $45^\circ$, and $90^\circ$, the responses are comparable to that of 20C-H composites. At $\theta =$
0°, both composites exhibited catastrophic-type and progressive-type failure behaviors, whereas progressive-type failure at $\theta = 45^\circ$ and at $\theta = 90^\circ$.

**Figure 71:** Uniaxial compressive response of ice-templated 30C-H composites for $\theta$ (a) 0°, (b) 45°, and (c) 90°. Similarly, uniaxial compressive response of ice-templated 30C-L composites for $\theta$ (d) 0°, (e) 45°, and (f) 90°. Legends represent porosity in the composites.
For a clearer comparison of strength across the composites, we show the variation of $\sigma_p$ of composites in Figure 80(a-c), and the gray shaded region in (a-c) represents upper and lower bounds of yield strength of pure epoxy. We also show the variation of maximum compressive strength of porous ceramics with $\theta$ in Figure 80(d-f). At $\theta = 0^\circ$, all the composites have overlapping strength. However, strength of some of the 30C-H composite specimens well exceeded 700 MPa, which is the upper limit of strength in 20C-H composites. At the same orientation, the strength range of 30C-L composites is observed to be lower than that of 30C-H composites, but comparable to that of 20C-H composites. At $\theta = 45^\circ$, the strength range is comparable for all the composites. Whereas, at $\theta = 90^\circ$, the strength of 30C-H and 30C-L composites is higher than that of 20C-H composites. Figure 80 also reveals that with increasing $\theta$ strength of both composites and porous ceramics decreased substantially, suggesting a strong correlation between the strength of these materials. The similarity in the variability of strength further reinforces the correlation.
Figure 72: Variation of maximum compressive strength ($\sigma_p$) with $\theta$ of ice-templated (a) 20C-H, (b) 30C-L, and (c) 30C-H composites. Similarly, variation of $\sigma_p$ with $\theta$ of ice-templated (d) 20P-H, (e) 30P-L, and (f) 30P-H porous ceramics.

In Figure 81, we show the variation of $\sigma_p$ of composites and porous ceramics with ceramic content for $\theta$ of 0° (Figure 81a), 45° (Figure 81b), and 90° (Figure 81c). We make several insightful observations from this figure. At $\theta = 0^\circ$, despite having a 10% difference in ceramic content, the strength of 30P-L ceramics is only marginally higher than that of 20P-H ceramics. Whereas, for a 6% difference in ceramic content, the strength of 30P-H ceramics is much higher than that of 30P-L ceramics. Thus, at $\theta = 0^\circ$ strength governing factor is not necessarily the ceramic content but the morphology of porous ceramics, otherwise the strength of 30C-L would be
significantly higher than that of 20C-H. The 30P-L and 20P-H ceramics have comparable strength because of the similar morphology (lamellar), and hence the corresponding composites also exhibited comparable strength. Significant strength increase from 30P-L ceramics to 30P-H ceramics is attributed to the change in the morphology from lamellar to dendritic, rather than the porosity difference. Hence, strength increase from 30C-L composites to 30C-H composites is also attributed to the inherent morphology difference between the porous ceramics. At $\theta = 45^\circ$, strength increased from 20P-H to 30P-L to 30P-H, but the strength data of the corresponding composites do not exhibit any clear trend. At $\theta = 90^\circ$, porous ceramics exhibited a similar trend in strength, and strength of 30C-L and 30C-H composites is higher than that of 20C-H composites. Figure 81 indicates that the strength of ice-templated composites is less sensitive to ceramic content but is strongly influenced by the morphology of porous ceramic. In ice-templated composites, it is expected that ceramic phase will govern the compressive response at $\theta = 0^\circ$, whereas polymer phase will dominate the response at $\theta = 90^\circ$, and strength will decrease from $\theta = 0^\circ$ to $\theta = 90^\circ$. The current results are in strong agreement but also revealed an abrupt decrease of strength with $\theta$. The strength of porous ceramics at $\theta = 0^\circ$ is significantly lower ($< 20$ MPa) compared to that of composites and epoxy and decreased further ($< 5$ MPa) at higher $\theta$ values. Thus, the strength of porous ceramics was enhanced remarkably upon infiltration with epoxy, and the strength advantage of composites was well maintained up to $\theta = 10^\circ$. However, uncertainty in failure type accompanies the strength advantage.
Figure 73: Variation of maximum compressive strength of ice-templated composites and porous ceramics with ceramic content at (a) $\theta = 0^\circ$, (b) $\theta = 45^\circ$, and (c) $\theta = 90^\circ$.

### 7.3.3 Weibull statistical analysis and deformation characteristics of ice-templated ceramics

The two-parameter form of Weibull equation which describes the probability of failure ($P_f$) for a given uniaxial stress $\sigma$ is [162]

$$1 - P_f = \exp\{- (\sigma / \sigma_o)^m\},$$  \hspace{1cm} (1)

where $\sigma_o$ is a scaling parameter, referred to as a characteristic strength defined as the stress at which $P_f$ is 63.2%, and $m$ is the Weibull modulus. Probability of failure is estimated as

$$P_{f,i} = (i - 0.5) / n,$$  \hspace{1cm} (2)

where $n$ is the total number of samples tested, and $i$ is the sample rank in ascending order of failure stress. The double logarithmic form of the Weibull expression is

$$\ln \ln[1 / (1 - P_f)] = m \ln \sigma - m \ln \sigma_o.$$  \hspace{1cm} (3)
By fitting a straight line to the data of \( \ln \ln [1/(1 - P_f)] \) vs. \( \ln \sigma \), we obtain the Weibull modulus \( m \) from the slope of the straight line and the scaling parameter \( \sigma_0 \) from the intercept. The higher the value of \( m \), the smaller is the variability of failure strength. Figure 82 shows plots of \( \ln \ln [1/(1 - P_f)] \) vs. \( \ln \sigma \) for different \( \theta \) for the composites (a-c) and porous ceramics (d-f).

**Figure 74:** Weibull statistical analysis for (a-c) ice-templated composites and (d-f) ice-templated porous ceramics. Each legend indicates the layer orientation (\( \theta \)), Weibull modulus (\( m \)), and characteristic strength (\( \sigma_0 \), MPa).
For 20C-H composites, at $\theta = 90^\circ$ $m$ is 10.2, whereas at all other $\theta$ $m$ values are within 4.3-5.9. For 30C-L composites, $m$ values for $\theta$ of 0°, 45°, and 90° are 3.8, 5.7, and 4.4. Similarly, for 30C-H composites, $m$ values for $\theta$ of 0°, 45°, and 90° are 3.9, 6.9, and 6.1. The low $m$ values indicate the significant variability in strength, irrespective of ceramic content, $\theta$, and failure type. The Weibull analysis for ice-templated ceramics shows even high variability of strength (lower $m$ values). Therefore, the Weibull statistical analysis reinforces that failure of the composites is inherently related to the failure of porous ceramics. Fracture in ice-templated ceramic structure instigated failure in ice-templated composite, suggesting that failure in the templated ceramic network is a strength-limiting factor in the failure of composites.

At this juncture, we shed insights into the deformation and failure characteristics of ice-templated porous ceramics for different directions of compressive loading, which is related to the failure in composites. According to Gibson and Ashby models [95], compressive strength ($\sigma$) of brittle cellular solids is related to $\rho_r$ as

$$\frac{\sigma}{\sigma_s} \propto \rho_r$$  \hspace{1cm} (for closed-cell, brittle crushing), \hspace{1cm} (4)$$

$$\frac{\sigma}{\sigma_s} \propto (\rho_r)^{1.5}$$  \hspace{1cm} (for open-cell, brittle crushing), \hspace{1cm} (5)$$

$$\frac{\sigma}{E_s} \propto (\rho_r)^3$$  \hspace{1cm} (for honeycomb, out-of-plane deformation, elastic buckling), \hspace{1cm} (6)$$

$$\frac{\sigma}{E_s} \propto 0.22(\rho_r)^3$$  \hspace{1cm} (for honeycomb, in-plane deformation, elastic buckling), \hspace{1cm} (7)$$

and

$$\frac{\sigma}{\sigma_s} \propto (\rho_r)^2$$  \hspace{1cm} (for honeycomb, in-plane deformation, brittle crushing). \hspace{1cm} (8)$$

Here, $\sigma_s$ and $E_s$ are compressive strength and Young’s modulus, respectively, of cell wall material. For in-plane deformation in honeycomb (loading perpendicular to the axis of hexagonal cells), cell walls bend and give rise to linear elasticity (provided the wall material is itself linear elastic) [95].
Beyond a critical strain, the cell walls will collapse and set the limit for strength. Honeycombs exhibit a much stiffer and stronger response when compressed parallel to the axis of the hexagonal cell (out-of-plane compressive deformation). For this direction of loading, cell walls suffer compression (experience significant axial deformation, as well as shear), and the collapse stress is much higher than in-plane deformation [39]. Note that for equations (6) and (7), out-of-plane and in-plane compressive deformation in honeycombs, respectively, elastic buckling of cell walls is the strength-limiting factor [95]. Strength prediction for the out-of-plane brittle failure of honeycombs (assuming defect-free cell walls) [95] significantly exceeds the strength prediction of closed-cell foam by brittle crushing and is thus not shown here.

**Figure 75:** Variation of maximum compressive strength ($\sigma_p$) of ice-templated sintered Al$_2$O$_3$ materials, normalized by flexural strength of sintered bulk Al$_2$O$_3$ (510 MPa), with relative density ($\rho_r$).
Figure 83 compares the variation of $\sigma_p$ of ice-templated porous ceramics (normalized by the flexural strength of sintered, dense $\text{Al}_2\text{O}_3$, 510 MPa [163]) with $\rho_r$ to the model predictions (dotted lines). Strength data at $\theta = 0^\circ$ of 20P-H porous ceramics are mostly concentrated around the model prediction for the out-of-plane compressive deformation of honeycombs, equation (6). For 30P-L porous ceramics, the strength of materials at $\theta = 0^\circ$ is also in a reasonable agreement with equation (6). Whereas, for 30P-H, the strength at $\theta = 0^\circ$ seems to outperform the prediction by equation (6) and approaches the strength of the closed-cell foams. The trends in the strength of porous solids that we observe at $\theta = 0^\circ$ are consistent with few previous reports [42,55,140]. Ceramic lamella walls in ice-templated ceramics do not collapse in a pure axial fashion; otherwise, their strength would well surpass that predicted for closed-cell foam (brittle crushing). The primary origin of similarity between the experimental data and predicted data by equation (6) is that for ice-templated material at $\theta = 0^\circ$ and out-of-plane compressive deformation of honeycomb, walls are parallel to the direction of compression and axial (elastic) deformation of the walls is a dominant mechanism. Lamella walls carry compressive load axially; however, an instability in the walls during axial deformation, possibly by buckling, limits the load-bearing capacity [49,50,138]. At $\theta = 0^\circ$, a similar axial mode of deformation also dominates in the walls of 30P-H materials. With increasing $\rho_r$, the compressive strength of honeycomb increases due to the increase of cell wall thickness, enhancing the resistance of the walls to axial deformation [95]. However, the strength of 30P-H materials well outperformed that of predicted for honeycombs (out-of-plane deformation, elastic buckling). We conjecture that an increase in the density of lamellar bridges in these materials significantly enhanced the axial load-bearing capacity of lamella walls, and the strength of these materials surpassed the model prediction. At $\theta = 45^\circ$, strength data are in the vicinity of model prediction for the in-plane compressive deformation of honeycomb, equation
Whereas, at $\theta = 90^\circ$, the measured strength values are well below that predicted by equation (7). Note that strength values at $\theta = 45^\circ$ and $\theta = 90^\circ$ are well below that predicted for honeycomb in-plane deformation by brittle crushing, equation (8). Since, at $\theta = 90^\circ$, ice-templated materials underperform compared to the model prediction for in-plane deformation where walls experience bending, we suggest that another deformation mechanism contributes to driving down the strength.

**Figure 76:** Schematics showing lamella walls in ice-templated porous ceramics at different orientations (a) $0^\circ$, (b) $45^\circ$ and (c) $90^\circ$ relative to compression direction. In each figure, microstructure contains multiple domains, and all the lamella walls are parallel to the growth direction. For simplicity, lamellar bridges are not shown in the schematics. In each figure, the yellow shaded surface indicated as “image plane” represents the specimen surface that was imaged during compression test.

In Figure 84, we show schematics of lamella walls in ice-templated ceramics at different orientations relative to the loading direction. In these simplified schematics, all the walls are parallel to the growth direction of ice crystals, and lamellar bridges are not shown. There are multiple domains, and each domain contains a set of lamella walls. In each figure, the shaded surface represents the surface that was imaged during the compression test (discussed in the next
section). At $\theta = 0^\circ$, all the walls are parallel to the compressive loading direction and most favorably oriented to carry the applied load axially (Figure 84a). Thus, lamella walls will exhibit maximum resistance to buckling and hence maximum compressive load-bearing capacity. With the increase in $\theta$, lamella walls undergo sliding over one another due to the shear and bending contribution of the walls to macroscopic response increases with the contribution being maximum at $\theta = 90^\circ$ [95]. Even for a moderate tilting of lamella walls relative to the loading direction, the efficiency of the walls to axially carry the load can deteriorate significantly and hence compressive strength. Due to the contributions of both shear and bending of walls, ice-templated materials at $\theta = 90^\circ$ exhibit response weaker than that predicted by equation (7).

7.3.4 Direct visualization of damage evolution in ice-templated composites

Optical images in Figures 85 ($\theta = 0^\circ$) and 86 ($\theta = 45^\circ$ and $\theta = 90^\circ$) at different strains reveal damage evolution in the composites. Our discussion is based on the observations made from the specimen surfaces that were imaged, and for each composition and orientation at least three specimens were imaged. The selected optical images are, however, representative of damage evolution in these composites. Some of the optical images are relatively darker due to the excessive spray of black paint. Stress-strain curves in Figures 85a and 85b correspond to catastrophic-type and progressive-type failure in 20C-H composites, respectively, at $\theta = 0^\circ$. At the end of the elastic limit, several cracks developed (damage initiation) in the specimen, propagated approximately parallel to the loading direction and caused axial splitting (formation of columnar fragments) of the specimens. Although 20C-H composites exhibited distinctly different failure behaviors at the macroscopic level (as reflected in the stress-strain curves), the failure mechanism at the microscopic level is axial splitting. A distinct difference at the microscopic level, however, is that
for the catastrophic-type failure response, crack propagation caused an immediate burst in the specimen, and the specimen was severely fragmented. Within the axial (columnar) fragments, cracks developed in the horizontal direction as well (image #4, Figure 85a) and caused the "mushrooming" of the specimen, which can account for the sudden loss of load-bearing capacity.
Figure 77: Damage evolution and failure at $\theta = 0^\circ$ in (a-b) 20C-H, (c-d) 30C-L, and (e-f) 30C-H composites.
For progressive-type of failure, crack propagation is gradual and did not cause an abrupt failure in the material. Even after severe deformation, the recovered specimens were partially intact. In the 30C-L composite specimens (Figures 85c and 85d), the evolution of multiple cracks running parallel to the loading direction and axial splitting of specimens are significantly prominent. The optical images reveal the development of multiple vertical fragments (columnar fragments) and subsequently tilting of the fragments relative to the loading direction. While the stress-strain curves for 30C-L composites suggest a noticeable difference in the failure behavior, the optical images revealed a comparable mechanism (axial splitting) of damage evolution at the microscopic level. For the 30C-H composites (Figures 85e and 85f), the axial splitting is significantly less prominent compared to the other composites, and again the process of failure is comparable, irrespective of the differences in the stress-strain curves. In the progressive-type failure regime, deformation in all the composites occurred at a stress level that is well above the stress required for plastic deformation in epoxy. Thus, although there are some differences in the compressive stress-strain curves indicating catastrophic-type failure vs. progressive-type failure, at a relatively microscopic level damage evolution process is not distinctly different. However, when damage initiated at a relatively high-stress level, the material immediately exploded into fragments and lost the load-bearing capacity. Whereas, when damage initiated at a relatively low-stress level, the material was able to prevent abrupt failure. We suggest that these differences at the microscopic level resulted in the differences in failure response at the macroscopic level (stress-strain curves).

At $\theta = 45^\circ$, with increasing deformation in the stress plateau regime, cracks propagated at an angle approximately $45^\circ$ relative to the loading direction. Figure 86a shows that the first few cracks developed (image #2), and with increasing deformation, the number of cracks also
increased. While the cracks are almost at 45⁰ to the loading direction, cracks are almost perpendicular to each other. Few cracks stopped at the interfaces of other cracks. At θ = 90⁰ as well, all the composites exhibited similar characteristics of failure. Cracks developed at approximately 45⁰ (and close to that) to the loading direction, and few cracks stopped at the boundary of other cracks.

**Figure 78:** Damage evolution and failure at θ = 45° in (a) 20C-H, (b) 30C-L, and (c) 30C-H composites. Similarly, damage evolution and failure at θ = 90° in (d) 20C-H, (e) 30C-L, and (f) 30C-H composites.
Investigation of cracks in deformed specimens through microstructural analysis is beyond the scope of this work, and we will address that in a separate communication. However, here, we refer to Figure 84 to shed some insights. At $\theta = 0^\circ$, the formation of cracks parallel to the loading direction could be related to the delamination at the Al$_2$O$_3$-epoxy interfaces. Figure 85 revealed that the formation of cracks and axial splitting is more prominent in the 20C-H and 30C-L composites than the 30C-H composites. Recall that 20P-H and 30P-L porous ceramics have lamellar morphology, and hence the corresponding composites are composed of relatively long, straight Al$_2$O$_3$-epoxy interfaces. Crack propagation along the interfaces is expected to be less hindered (due to the lack of connectivity across the walls) in the 20C-H and 30C-L composites. As a result, these materials exhibited prominent development of interfacial cracks running parallel to the growth direction of ice crystals and axial splitting. On the other hand, the morphology of 30P-H porous ceramics is highly dendritic, which enhances pore tortuosity and tortuosity of Al$_2$O$_3$-epoxy interfaces, and hence the tortuosity of the crack path in the infiltrated composites. Interfacial crack propagation is expected to be harder in 30C-H composites than in the other composites, and the development of axial cracks parallel to the loading direction will be less prominent. This is consistent with that the strength of 30C-H composites is higher compared to that of the other two composites. At $\theta = 45^\circ$, the formation of cracks at 45$^\circ$ relative to the loading direction suggests shear-induced deformation in the composites. While the formation of cracks at 45$^\circ$ to loading direction suggests crack opening at the Al$_2$O$_3$-epoxy interfaces, note that cracks are also perpendicular to each other. Thus, some cracks are not necessarily along the Al$_2$O$_3$-epoxy interfaces but developed perpendicular to those interfaces. At $\theta = 90^\circ$, we imaged the specimen surface that is indicated in Figure 84c. Due to shear-induced deformation, if cracks open up at the
Al₂O₃-epoxy interfaces within different domains, two of the four specimen surfaces (parallel to the loading direction) will exhibit cracks formed at angles similar to that observed in Figure 86.

7.3.5 Theoretical estimation of compressive strength of ice-templated composites

We estimated upper and lower bounds of the strength of composites over the θ range of 0 – 90⁰. According to the Tsai-Hill failure criterion, off-axial strength (σₚ) of an orthotropic composite at an arbitrary angle θ is given as [11,45]:

\[
\frac{1}{\sigma_p^2} = \frac{1}{\sigma_L^2} (\cos^4 \theta - \sin^2 \theta \cos^2 \theta) + \frac{1}{\tau_s^2} (\sin^2 \theta \cos^2 \theta) + \frac{1}{\sigma_T^2} (\sin^4 \theta) \tag{9}
\]

Here, σₗ is the longitudinal strength (θ = 0⁰) and σₜ is the transverse strength (θ = 90⁰) of the composite. Whereas, τₛ is the in-plane shear strength of the composites. To estimate upper and lower bounds of σₚ, we also need to consider the upper and lower bounds for σₗ, σₜ, and τₛ.

For a composite consisting of alternate layers of hard and soft phases, σₗ corresponds to the failure of the hard phase and is expected to rely significantly on the strength of the hard phase. Using the equal-strain Voigt hypothesis (i.e., the rule of mixtures), we can estimate σₗ as [29,42,49,146]:

\[
\sigma_L = \sigma_{\text{epoxy}} V_{\text{epoxy}} + \sigma_{\text{Al}_2\text{O}_3} V_{\text{Al}_2\text{O}_3}, \tag{10}
\]

where σₑpoxy and σₑAl₂O₃ are the failure strength of bulk epoxy (83.2 MPa) and Al₂O₃, respectively. Similarly, Vₑpoxy and VₑAl₂O₃ are volume fractions of epoxy and Al₂O₃ phases, respectively, in the composite. We estimated upper and lower bounds of σₗ based on the failure characteristics of ceramic lamella walls [42]. The upper limit of σₗ corresponds to a scenario where epoxy provides rigid mechanical support to the ceramic lamellae to the extent that the ceramic walls fail in pure compression, without experiencing any buckling-induced elastic instability. For this scenario, we considered the compressive strength of bulk Al₂O₃ (2.5 GPa) as σₑAl₂O₃ [148]. On the other hand,
we attribute the buckling-induced failure of ceramic walls by bending to the lower limit of \( \sigma_L \) and considered bend strength (\( \sigma_b \)) of bulk Al\(_2\)O\(_3\) (510 MPa) as \( \sigma_{Al_2O_3} \) [163]. At \( \theta = 90^0 \), the compressive strength of ice-templated composites is as low as the yield strength of pure epoxy and as high as 200 MPa. It is possible that the lower end of \( \sigma_T \) corresponds to the yielding of epoxy, whereas the higher end of \( \sigma_T \) is related to the fracture of ceramic lamella walls due to bending. Thus, we considered \( \sigma_{epoxy} \) as the lower limit of \( \sigma_T \), whereas \( \sigma_b \times V_{Al_2O_3} \) (\( V_{Al_2O_3} \) is used as a knockdown factor) as the upper limit of \( \sigma_T \). We assumed \( \tau_s \) as half of the compressive strength of composites (maximum resolve shear stress is half of the axial stress) and considered upper and lower bounds of \( \sigma_T \) [164,165]. Thus, the upper limit and lower limit of \( \tau_s \) are \( (\sigma_b \times V_{Al_2O_3})/2 \) and \( \sigma_{epoxy}/2 \), respectively. Upper and low bound values of \( \sigma_L, \tau_s, \) and \( \sigma_T \) are listed in Table 3. In ice-templated ceramics, lamella walls do not develop precisely parallel to the applied temperature gradient, and the walls are also not perfectly parallel to each other [166]. As shown in Figure 87, the analysis of the SEM images along the growth direction of ice crystals revealed that orientation mismatch could be easily several degrees, which is expected to affect strength. For example, at \( \theta = 0^0 \), all the lamella walls are not perfectly parallel to the loading direction, which will reduce the strength. Therefore, strength estimated using equation (9) for a given angle should be corrected, and we considered a tilt of 3\(^0\). As an example, strength estimated for \( \theta = 3^0 \) was considered as the strength at \( \theta = 0^0 \). Our calculations showed that beyond \( \theta = 15^0 \), there was practically no difference in strength values with and without tilt correction. In Table 4, we listed strength values of upper bounds with and without tilt correction for \( \theta = 0^0, \theta = 5^0, \theta = 10^0, \) and \( \theta = 15^0 \).
Table 9: Maximum and minimum values for upper bound and lower bound of longitudinal strength ($\sigma_L$), shear strength ($\tau_s$), and transverse strength ($\sigma_T$).

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<th>Composite ID</th>
<th>Stress components</th>
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<td>$\tau_s$</td>
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<td>$\sigma_T$</td>
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Table 10: Comparison of maximum predicted strength ($\sigma_p$) of composites without and with tilt of 3° in lamella walls.

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<td>856.9</td>
</tr>
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<td></td>
<td>With tilt</td>
<td>750.3</td>
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<tr>
<td>30C-L</td>
<td>No tilt</td>
<td>1144.2</td>
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<td></td>
<td>With tilt</td>
<td>1012.4</td>
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<tr>
<td>30C-H</td>
<td>No tilt</td>
<td>1320.6</td>
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<td></td>
<td>Tilt</td>
<td>1171.2</td>
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Figure 79: (a) A representative SEM micrograph of ice-templated Al$_2$O$_3$ revealing lamella walls along the ice-growth direction. (b) Frequency distribution of orientation ($\theta$) of walls. (c) Variation of the orientation of walls measured from different SEM images.

Figure 88 shows the comparison between experimental strength values and predicted strength values for 20C-H (Figure 88a), 30C-L (Figure 88b), and 30C-H (Figure 88c) composites. For each composite (20C-H / 30C-L / 30C-H), there is a variation of ceramic content in the specimens, which was accounted for in the estimation of upper bound (green band) and lower bound (orange bound) of strength. The general trend in the experimental data is well predicted, with the experimental data mostly residing within the upper and lower bounds. Although for 30C-L and 30C-H composites, we performed compression tests at only three orientations, the strength of these composites for other orientations should be within the bounds (or slightly outside).

The curve for upper bound shows a drastic drop in strength within a narrow $\theta$ range of 0 – 15° but a gradual change beyond 20°. On the other hand, the curve for lower bound shows a gradual change of strength over the entire $\theta$ range. The upper bound of $\sigma_L$ is markedly higher compared to
the upper bound of $\tau_s$ and $\sigma_T$, which is, however, not the case for lower bound values. Therefore, with increasing $\theta$ as the contribution of $\tau_s$ and $\sigma_T$ increases and the contribution of $\sigma_L$ decreases, strength drops drastically for the upper bound curve but gradually for the lower bound curve. This also suggests that the higher the ratio of $\sigma_L$ to $\sigma_T$ (i.e., strength anisotropy with $\sigma_L > \sigma_T$), the higher is the strength decrease with $\theta$. For ice-templated ceramic-polymer composites, the strength anisotropy will mainly depend on the longitudinal strength of composite and thus on the failure mechanism of ceramic walls, such as pure compression failure vs. bending failure.

At any $\theta$, the distribution of measured strength values between the upper and lower bounds strongly suggests the influence of competitive mechanisms on the failure of composites. Close to the growth direction of ice crystals, the competition between failure mechanisms in ceramic walls (pure compression vs. bending) will strongly influence strength (and variation) and both mechanisms contribute to failure. Due to the misalignment and variation of thickness from wall to wall and along the growth direction, the compressive loading scenario in ice-templated ceramics is complex. At $\theta = 0^\circ$, lamella walls can experience axial deformation and bending, as well as shear. In specimens, where the walls (or majority of them) are more favorably aligned relative to the loading direction, the specimens can better sustain the compressive load axially and exhibit higher strength, approaching the upper bound. Whereas, in specimens with walls are less favorably aligned relative to the loading direction, bending (and shear) contribution increases, which lowers the strength and the strength approaches the lower bound. The predicted upper bound of strength for 30C-L and 30C-H at $\theta = 0^\circ$ is significantly higher compared to that of 20C-H, which is mainly due to the increased contribution of ceramic fraction in the former composites and the corresponding increased contribution of pure compression failure. We can observe that the higher end of measured strength values in both 20C-H and 30C-H at $\theta = 0^\circ$ is in good agreement with the
predicted upper bound. Recall from the discussion in Section 3.3 that buckling resistance in 30P-H materials is significantly higher than in 20P-H. Therefore, strength increase from 20C-H to 30C-H is consistent with the increase in buckling resistance in the corresponding porous ceramics. For 30C-L, the maximum measured strength is much lower than the predicted upper bound, attributed to the lamellar morphology and weak buckling resistance of ceramic walls.

**Figure 80:** Comparison of experimental data and predicted data for compressive strength of (a) 20C-H, (b) 30C-L, and (c) 30C-H composites. Green and orange bands represent upper bound and lower bound, respectively, of strength. In each color band and at a given \( \theta \), maximum and minimum strength correspond to the maximum and minimum ceramic volume fraction, respectively, in composite.

With the increase in \( \theta \), the gap between upper and lower bounds decreases, mainly because of the decreased contribution of pure compression failure in estimating the upper bound. Figure
suggests that as we move away from $\theta = 0^\circ$, bending failure of ceramic walls, shear failure at interfaces, and compressive yielding in epoxy become the dominant factors in determining the strength of ice-templated composites. In fact, in the $\theta$ range of $15^\circ – 90^\circ$, the shear failure and yielding in epoxy are strength weakening mechanisms. Whereas, failure by bending of ceramic walls contributes to enhancing strength. This work revealed significant variability in the strength of composites, suggesting the role of competitive mechanisms in failure. We showed that from the knowledge of composition, compressive and bend strength of the ceramic phase, and yield strength of the polymer phase, upper and lower bounds of the strength of ice-templated composites can be determined, which will encompass the strength of composites.

7.4 Significance for designing materials with structural gradient

This work was motivated by the structural gradient that we observe in natural materials and investigated the influence of the loading direction on the compressive response of ice-templated multilayered $\text{Al}_2\text{O}_3$-epoxy composites. Although this investigation is not on the development of multilayered ceramic-polymer composites with a structural gradient, the current results will be useful to understand the mechanical behavior of multilayered strong-tough composites with structural gradient and designing such materials. When a multilayered composite with a continually varied layer orientation is subjected to compressive loading, the material response at different regions within the structure at the microscopic level will vary. To understand the overall macroscopic response of such materials, it is essential to characterize the compressive response of the individual elementary structural units within which structural gradient is absent and thus generate piecewise information. Each structural unit will have a specific layer orientation relative to a global loading direction. From ice-templated sintered porous ceramics, we extracted specimens at different orientations relative to the growth direction of ice crystals and infiltrated
the specimens with a polymer phase to develop composites. Thus, at each orientation, the compressive mechanical response of the composite specimens represents the response of a structural unit with a specific layer orientation relative to the global loading direction. Different compressive responses measured across the structural units provide significant insights into the role of various factors in governing the strength.

In Fig. 89, we have summarized the current results and illustrated the factors that govern the uniaxial compressive strength of ice-templated composites. The yellow shaded region shows the strength variation with θ and includes upper and lower bounds of strength. We now briefly discuss the significance of the current results to design multilayered ceramic-polymer composites with a structural gradient. There are two regimes: regime A (θ = 0 – 10°), strongly ceramic dominated, and regime B (θ > 10°), weakly ceramic dominated. In these materials, the regions in the structure with layer orientation close to the compressive loading direction (regime A) are the potential areas that can exhibit maximum resistance to compressive deformation. However, the primary criterion is that ceramic walls must resist failure by bending (which can cause elastic instability and premature failure). Rigid mechanical support by epoxy layers is crucial to maximizing the compressive load-bearing capacity of ceramic walls, creating favorable conditions for failure by pure compression, which requires significantly higher stress for failure than that in bending. Factors such as the reduced misalignment between ceramic walls, uniform thickness of ceramic walls, and rigidity of the polymer phase will favor compression failure. Our results suggest that merely increasing the ceramic fraction in multilayered composites could be insufficient for strength enhancement. The connectivity between ceramic walls should also be increased to reduce the propensity of failure by bending. However, the strength enhancement can also increase the propensity of catastrophic-type failure in these composites.
Moving to the regions with \( \theta \) just above \( 10^\circ \) (regime B), compressive strength is dramatically reduced. However, the materials will exhibit mostly progressive-type failure where the polymer phase will undergo plastic deformation, and ceramic walls will gradually fracture; both will attribute energy absorption capacity (toughness). In this regime, shear failure of ceramic-polymer interfaces and yielding in the polymer are strength weakening mechanisms, whereas the contribution from bending failure of ceramic walls can attribute strengthening. Between \( 45^\circ – 90^\circ \), compressive strength will depend significantly on the ceramic fraction but less on the connectivity between ceramic walls. Although stiffness was not estimated, it is expected that the regions with higher strength will also exhibit greater stiffness. The current results are significant in understanding the mechanical behavior of and designing multilayered strong-tough composites with a structural gradient. Different regions in the structure will respond differently to an applied compressive load with a significant variation in strength and failure behavior (brittle-like failure vs. ductile-like failure).
**Figure 81:** Schematic representation of the influence of loading direction relative to layer orientation on uniaxial compressive strength of multilayered ceramic-polymer composites. The yellow shaded region shows the strength variation with θ and includes the upper bound and lower bound of compressive strength of ice-templated composites. In regime A (0 – 10°), compressive strength is strongly dominated by failure of characteristics of ceramic walls (compression failure vs. bending failure). In regime B (θ > 10°), bending failure of ceramic walls, shear failure at interfaces, and compressive yielding in epoxy are the dominant factors in governing the strength. Blue and red arrows suggest the contribution of different factors in increasing and decreasing, respectively, strength of composites.
7.5 Conclusions

This study investigated the influence of loading direction on the compressive response of ice-templated alumina-epoxy composites. Ice-templated alumina materials were developed from suspensions of different compositions and at relatively high and low freezing front velocities. From sintered porous ceramics, specimens were extracted at different orientations relative to the growth direction of ice crystals. Porous alumina specimens were infiltrated with epoxy to develop composites. Changes in composition and freezing front velocity resulted in composites with varying ceramic content and morphology. For comparison, the compressive response of porous ceramics was also measured. The results revealed a strong dependence of compressive strength and failure behavior on the loading direction relative to the growth direction of ice crystals. Along the growth direction, composites exhibited either high strength with brittle-like (catastrophic) failure or low strength with ductile-like (progressive) failure. Away from the growth direction, failure became more ductile-like, strength decreased gradually, and material response became increasingly comparable to that of epoxy. The strength of both porous ceramics and composites is dependent on ceramic content and morphology and exhibited significant variability. Weibull modulus analysis indicated a strong correlation between the strength of ice-templated porous ceramics and ice-templated composites. The direct visualization revealed the role of ceramic content, morphology, and loading direction on the deformation and failure characteristics of composites. The Tsai-Hill failure criterion for off-axial strength of an orthotropic composite was used to evaluate the role of competitive failure mechanisms on the compressive response of ice-templated composites. From the knowledge of composition, compressive and bend strength of the ceramic phase, and yield strength of polymer phase, upper bound and lower bound of strength
were predicted, which encompassed the strength of composites. Finally, the significance of the results in designing materials with a structural gradient was briefly discussed.

Acknowledgment

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CHAPTER 8

DEFORMATION MECHANISMS IN ICE-TEMPLATED ALUMINA–EPOXY COMPOSITES FOR THE DIFFERENT DIRECTIONS OF UNIAXIAL COMRESSIVE LOADING

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8.1 Introduction

Natural hybrids such as seashells, bone, teeth, fish scales, and lobster cuticle provide major bioinspiration to the fabrication of novel hierarchical composites with improved mechanical and functional properties [2,11–15,167,168]. Many of these natural composites exhibit multilayered architecture with alternate layers of hard (brittle) and soft (ductile) phases. The natural mineralized composites are composed of components that have relatively poor intrinsic mechanical properties. However, the strength and toughness of the natural composites far exceed those of their material constituents, and that predicted by the rule of mixture. The origin of superior properties in natural hybrids is inherently related to the complex hierarchical organization of the components encompassing multiple length-scales. However, a profound challenge is to develop suitable fabrication techniques that enable us to mimic the complex features of the hierarchical microstructure of natural composites into engineering materials [2]. Toward this end, freeze-casting, also known as ice-templating [22,38,41,50,77,169–171], enables the fabrication of
synthetic multilayered ceramic-based composites and thus has gained significant attention for bioinspired materials development.

The central objective of this study is to uncover the inelastic deformation mechanisms that evolve in ice-templated Al₂O₃-epoxy composites for different directions of uniaxial compressive loading relative to layer orientation (also the growth direction of ice crystals). Recently, Akurati et al. [172] investigated the uniaxial compressive response of ice-templated Al₂O₃–epoxy composites for different loading directions relative to the growth direction of ice crystals, which revealed a strong strength anisotropy. Ice-templated composites exhibited the highest strength for loading direction parallel to the growth direction and catastrophic-type (brittle-like) failure. A drastic decrease in strength occurred for off-axis loading (i.e., loading direction away from growth direction), and composites exhibited progressive-type (ductile-like) failure. In the study by Akurati et al. [172], for each loading orientation, at least 15 specimens were tested, and Weibull modulus analysis revealed a similar level of strength variability for all loading orientations between 0°–90°. A theoretical analysis by Akurati et al. [172], based on the Tsai-Hill failure criterion [11,172], suggested that strength anisotropy in ice-templated composites is strongly related to the variation in the contributions of the individual phases (ceramic and polymer) to strength for different directions of loading. For load applied along the growth direction, ceramic (strong and brittle) phase governs the strength, and hence composite exhibited maximum strength and catastrophic-type failure. Away from the growth direction, as the contribution of polymer (weak and ductile) phase increased, strength decreased significantly, and composites exhibited progressive-type failure.

In the context of the findings by Akurati et al. [172], the current study reports experimental evidence that the primary inelastic deformation mechanisms that trigger failure in ice-templated
multilayered $\text{Al}_2\text{O}_3$–epoxy composites are strongly influenced by compressive loading orientation relative to the growth direction, vital knowledge for improved understanding of structure–mechanical property relationships and materials design. The effects of compression direction on deformation mechanisms were revealed by probing into the mechanisms for loading directions of $0^\circ$, $45^\circ$, and $90^\circ$ relative to the growth direction of ice crystals. This work studied the deformation mechanisms and damage by performing postmortem analyses of deformed ice-templated composites. For this purpose, for each specimen, a compression test was stopped in the vicinity of maximum stress to retrieve the specimen at the onset of damage. The retrieved partially deformed specimens were thoroughly investigated for deformation mechanisms and damage using a scanning electron microscope (SEM) and performing X-ray nano computed tomography (nano-CT) using a 3D X-ray microscope (XRM).

8.2 Experimental

8.2.1 Fabrication of ice-templated porous ceramics and composites

Ice-templated porous ceramics were fabricated from aqueous suspensions containing 20 vol.% ultrafine $\text{Al}_2\text{O}_3$ particles ($d_{50} = 300$ nm, APA-0.5 Sasol, Tuscan, AZ). First, a required amount of deionized (DI) water and measured quantity of $\text{Al}_2\text{O}_3$ particles were taken into a Nalgene bottle. To enable uniform dispersion of $\text{Al}_2\text{O}_3$ particles in DI water, 1 wt.% (of powder) anionic dispersant (Darvan-C, R.T. Vanderbilt Co, Norwalk, CT) was added. Each suspension was milled for 24 hours using zirconia ($\text{ZrO}_2$) spheres of diameter 5 mm. Next, 5 wt.% (of powder) binder, poly-(2-ethyl-2- oxazoline), was added, and an additional 1 hour of milling was performed at a lower rpm. After completing the mixing cycle, the suspensions were first sieved to separate the milling media and next de-aired under vacuum (pressure 0.1 MPa) for 30 minutes.
From the aqueous Al\(_2\)O\(_3\) suspensions, ice-templated ceramics were fabricated using a custom-made device [19]. The device requires a hollow Teflon tube (mold) to be placed on a thin (thickness 0.8 mm) steel plate (referred to as "Cold-finger"), and the mold is then filled with an aqueous ceramic suspension. In this work, a Teflon hollow tube with an inner diameter of 18.5 mm, an outer diameter 26 mm, and a height of 25 mm was utilized, and for the casting of each sample, the mold was filled up to 20 mm height with aqueous Al\(_2\)O\(_3\) suspension. Next, the suspension in the mold was solidified (with solidification direction bottom to top) by applying a unidirectional temperature gradient. For this purpose, the entire mold assembly was inserted inside liquid nitrogen (N\(_2\)) Dewar and placed above the surface of liquid N\(_2\). Once the Cold-finger temperature goes below 0 °C, the ice crystals start to nucleate at the bottom of the suspension in contact with the Cold-finger and grow vertically under the influence of the temperature gradient. Thermal insulation surrounding the outside of the Teflon mold ensures a unidirectional thermal gradient. In this device, by adjusting the distance between the Cold-finger and liquid N\(_2\), the unidirectional freezing front velocity (FFV, growth rate) of the ice crystals is controlled. In this study, all the samples were fabricated at a gap of 1 mm, which resulted in an average FFV of 28.4 ± 1.9 \(\mu\)m/s. Average FFV was estimated by dividing the sample height by the time required to complete the solidification process; solidification was considered to begin when the temperature on the Cold-finger reached 0 °C.

The solidified samples were freeze-dried (sublimation) in a freeze-dryer (2.5L, Labconco, Kansas City, MI) for 96 h at low pressure (0.014 mbar) and temperature (-50 °C), which resulted in porous ceramic samples. The green samples were sintered at 1550 °C for 4 hours in an air atmosphere inside a box furnace (KSL-1700X, MTI Corporation, Richmond, CA).
The sintered Al$_2$O$_3$ materials were approximately 17 mm in diameter and 15.6 mm in height. From each sample, a 6 mm $\times$ 6 mm $\times$ 3 mm specimen was extracted. As shown schematically in Figure 90a, porous ceramic specimens were extracted at three different angles, $\theta$ (0°, 45°, and 90°), relative to the growth direction of ice crystals. Thus, $\theta$ represents the angle between the direction of compression and the growth direction of ice crystals. Note that lamella walls in porous ceramics are also oriented along the growth direction of ice crystals. Therefore, $\theta$ represents the angle between loading direction and wall orientation as well.

The extracted sintered porous Al$_2$O$_3$ specimens were infiltrated with a low viscosity epoxy resin (EpoxiCure 2, Buehler, Lake Bluff, IL) to fabricate ice-templated Al$_2$O$_3$-epoxy composites. The following steps were performed for polymer infiltration and fabricated of composites. First, an epoxy resin was mixed with a slow curing agent (EpoxiCure 2 Hardener, Buehler). The mixture was then subjected to low pressure (0.1 MPa) inside a vacuum desiccator to remove any entrapped air bubbles. Next, a sintered porous Al$_2$O$_3$ specimen was placed in the epoxy-curing agent mixture, and infiltration was performed at low pressure (0.1 MPa) for 30 minutes. Next, the infiltrated specimen was removed and cured at room temperature for 24 h. For comparison, pure epoxy specimens were also prepared.

8.2.2 Materials Characterization

Ice-templated composites were compressed at a displacement rate of 0.5 mm/min (strain rate of $10^{-3}$/s) using a mechanical testing machine (MTS, ALLIANCE RF/300). In this setup, the upper compression platen is attached to a spherical seat for improved alignment and ensuring even pressure across the entire surface of the specimen. During each experiment, sample surfaces in contact with compression platens were well lubricated, creating a frictionless contact, and hence friction can be considered negligible.
For each loading orientation, compression tests were stopped after reaching the maximum load, and the retrieved specimens were characterized for the deformation mechanisms using both SEM and 3D XRM. Note that two composite samples were deformed for each loading direction, where one sample was analyzed using an SEM, and the other sample analyzed using a 3D XRM. As mentioned in the previous study by the authors [172], for each \( \theta \), at least 15 specimens were tested, which conclusively revealed that strength decreased significantly from \( \theta = 0^\circ \) to \( \theta = 45^\circ \). However, a moderate decrease was measured from \( \theta = 45^\circ \) to \( \theta = 90^\circ \). Therefore, although only 2 samples were tested for each \( \theta \) in the current work to investigate the deformation mechanisms, it is expected that the current findings are representative of the dependence of failure mechanism on \( \theta \) and the strength–deformation mechanism relationship in ice-templated composites.

As shown schematically in Figure 90b, the loading surface (perpendicular to the loading direction) and side surface (parallel to the loading direction) of the deformed specimens were investigated using a desktop SEM (Phenom Pure, Thermo Fisher Scientific) to reveal the deformation characteristics. For each deformed sample, only one loading surface and one side surface were investigated using SEM. To track the damages observed on the exterior surfaces into the interior regions, approximately 1 mm depth of material was removed from one of the loading surfaces and one of the side surfaces (Figure 90c). However, this step was performed only for the sample compressed at \( \theta = 0^\circ \). The material was removed from the surfaces by gently grinding with 600 grit silicon carbide (SiC) paper, and the surfaces were then polished using 1200 grit SiC paper and 6 \( \mu \)m and 3 \( \mu \)m diamond pastes. The surfaces were again investigated using SEM.

For each loading orientation, a small specimen (2 mm \( \times \) 3 mm \( \times \) 6 mm, Figure 90d) was also extracted from the deformed composite sample (6 mm \( \times \) 6 mm \( \times \) 3 mm), which was used to further study the deformation mechanisms using a 3D XRM (Zeiss Xradia 510 Versa), which
enabled to investigate the interior regions in the specimens. While nano-CT of undeformed specimens was not performed, the surfaces of composite specimens before compression tests were checked using SEM, which did not reveal any damage. The use of both SEM and XRM allowed us to gain a comprehensive understanding of failure mechanisms in ice-templated composites.

All the specimens for X-ray nano-CT were scanned using the following parameters: 80 kV X-ray source, 88 μA target current, and 2 s exposure time. The obtained data sets were reconstructed using XMR Reconstructor software. Each reconstructed data set consisted of 988 slices with a resolution of 1008 x 984 pixels with a pixel size of 1.2 μm. Image processing of X-ray tomography images was performed using Dragonfly 2020.1 (Object Research Systems, Montreal). To enhance the image quality for data sets obtained from nano-CT, image processing was performed on the 2D slices using contrast and shading compensation image filters applied sequentially before 3D rendering.
Figure 82: (a) Schematics showing that specimens of dimensions 6 mm × 6 mm × 3 mm were extracted from ice-templated sintered Al₂O₃ materials at three different θ (0°, 45°, 90°) relative to the growth direction of ice crystals. Schematics showing (b) loading surface and side surface and (c) interior regions of deformed composite specimen used for investigation of deformation characteristics using SEM. (d) A small specimen (2 mm × 3 mm × 6 mm) was extracted from deformed composite specimen for each θ for nano-CT for further investigation of deformation mechanisms. SEM images of ice-templated (e) sintered porous Al₂O₃ and (f) Al₂O₃–epoxy composite. (g) Uniaxial compression tests were stopped after reaching the maximum stress and
the stress-strain curves of the specimens for different $\theta$ used for SEM and 3D XRM are shown. Also, included stress-strain curve of pure epoxy.

Dragonfly's Deep Learning (DL) network was implemented to reveal the cracks present within the ceramic lamella walls of the deformed composite specimens. However, this step was performed for the deformed specimens of loading orientations of $\theta = 45^\circ$ and $\theta = 90^\circ$. First, ceramic lamella walls were segmented from data sets to create Regions of Interest (ROI’s). Next, multiple 2D slices from the ROI were used to manually locate the cracks within the lamella walls using ROI toolbar. Finally, the selected slices were used to train the inbuilt DL network. The trained DL network was next applied to all slices in the data set to segment the cracks within the ceramic lamella walls of deformed ice-templated composites. Finally, the selected slices were used to train a neural network architecture U-Net [173].

8.3 Results

8.3.1 Microstructure and compressive response

Figures 90e and f show the representative SEM images, revealing the microstructures of ice-templated porous sintered $\text{Al}_2\text{O}_3$ material and $\text{Al}_2\text{O}_3$–epoxy composite, respectively. The estimated average porosity of sintered $\text{Al}_2\text{O}_3$ materials was $69.4 \pm 0.9$ vol.%, and the density of the corresponding composite was $1.98 \pm 0.1$ g/cm$^3$. The maximum porosity in the composite specimens was only 3 vol.%. The porous material (Figure. 90e) is observed to have lamellar morphology with long elongated pores and negligible bridges between lamella walls. Figure 90f shows lamellar morphology of ice-templated composite with alternate layers of $\text{Al}_2\text{O}_3$ and epoxy.
As shown in Figure 90g, at $\theta = 0^\circ$, compressive strength is observed to be greater than 700 MPa. With the increasing $\theta$, strength decreased significantly, below 200 MPa. Thus, ice-templated Al$_2$O$_3$–epoxy composites exhibited the highest strength at $\theta = 0^\circ$, where Al$_2$O$_3$ (hard phase) dominated the strength. Whereas, away from the growth direction, strength decreased markedly due to the increasing contribution of the epoxy (soft) phase. It can be seen that for $\theta = 45^\circ$ and $\theta = 90^\circ$, the compressive response of composites approaches to that of the pure epoxy. More details of the influence of $\theta$ on the compressive response can be found in our previous work [172]. From the area in the elastic regime of a stress-strain curve, stored elastic strain energy ($U_e$) was calculated as $U_e = 0.5 \times \sigma \times \varepsilon$, where $\sigma$ and $\varepsilon$ are stress and strain, respectively, at the elastic limit. At $\theta = 0^\circ$, $U_e$ was in the range of 3.65 – 4.1 MJ/m$^3$. At $\theta = 45^\circ$, $U_e$ was in the range of 0.55 – 1.0 MJ/m$^3$. Similarly, at $\theta = 90^\circ$, $U_e$ was in the range of 0.39 – 1.22 MJ/m$^3$. The stored elastic strain energy is dissipated during fracture at peak stress. Therefore, at $\theta = 0^\circ$, at peak stress, ice-templated composites not only exhibited highest compressive strength but also dissipated maximum strain energy compared to the other loading orientations.

8.3.2 Deformation mechanisms for compression direction of $\theta = 0^\circ$

The SEM images in Figure 91 reveal the deformation characteristics on one of the side surfaces (parallel to the loading direction) of a partially deformed composite specimen. Figures 91b-d show higher magnification SEM images of the deformation features observed in Figure 91a. As indicated by the yellow boundary, a large region is observed where the walls are significantly tilted compared to the walls outside the boundary. The tilted band has propagated across the entire specimen. As indicated by yellow arrows in Figures 91a and b, severe delamination occurred along the Al$_2$O$_3$–epoxy interfaces resulting in longitudinal cracks (columnar splitting). Most of the
longitudinal cracks are contained within the tilted region. Compressive deformation also resulted in cracks that propagated across the interfaces and are at an angle to the loading direction (indicated by orange arrows in Figures 91a, c, and d). These cracks are linked to the longitudinal cracks. During the tilting of the regions with the growing longitudinal cracks, a part of each columnar region (formed due to delamination) separated from the regions above and or below it. As a result, cracks originated from the longitudinal cracks and propagated at an angle to the loading direction.
Figure 83: (a) SEM image revealing inelastic deformation features on the side surface (parallel to the loading direction) of a partially deformed composite specimen, $\theta = 0^\circ$. A large region is observed that is tilted relative to the loading direction, as indicated by the yellow boundary. (b-d) Higher magnification SEM images of some of the deformation features observed in (a). Yellow arrows point to the delamination cracks along $\text{Al}_2\text{O}_3$–epoxy interfaces, whereas orange arrows point to the cracks propagated across the interfaces.

The SEM image in Figure 92a reveals the deformation characteristics on the interior surface observed after material removal, showing a large, tilted band (within the yellow boundary). Figures 92b and 92c show higher magnification SEM images of damage at the boundary regions. The severity of cracking within the tilted band is significantly less, and the longitudinal cracks observed on the exterior surface were mostly absent. The tilted band resemblances to kink band (deformation band due to shearing instability), the formation of which has been reported to cause failure in unidirectional fiber-reinforced polymer composites with the compression load aligned with the fiber direction [174–177]. Kink band formation, also referred to as plastic micro-buckling, is the dominant mode of failure in compression in anisotropic composites triggered by the inherent fiber misalignment (a processing-induced defect) and plastic shear deformation in the matrix. Kink band formation has also been reported for other types of anisotropic composite materials, such as metallic nanolaminates [178]. In a recent study, Röthlisberger et al. [170] reported kink band formation in ice-templated tungsten (W)–copper (Cu) composite induced by uniaxial compression. The intrinsic characteristics of the materials that exhibit kink band formation upon subjected to compressive load are the presence of pronounced mechanical anisotropy, a set of planes along which the shear strength is very low, and regions of misaligned fibers or layers. For example, as
mentioned above, in unidirectional fiber-reinforced polymer composites or laminates, the kink band forms for the compressive loading direction parallel to the fibers or layers. This is because shear on a plane parallel to the fibers or layers requires much lower stress than shear along any other direction due to the lower strength of the soft matrix phase [178–180].
Figure 84: (a) SEM image of the side surface (after removal of about 1 mm material) revealing inelastic deformation features (mainly kink band) in the interior of a partially deformed specimen, $\theta = 0^\circ$. The kink band is observed to be relatively intact in the interior of the specimen compared to the exterior surface (Figure 91). (b-c) Higher magnification SEM images of the boundary regions of the kink band, revealing significant fracture within Al$_2$O$_3$ walls and rotation of epoxy walls.

In this failure mechanism, deformation localizes within the kink band, and multiple kink bands of different widths can also develop. Within the kink band region, the soft matrix phase material experiences severe plastic shear deformation (matrix yielding). The fibers can also curve if they can withstand the rotation during kink band formation; otherwise, they break. Similar microstructural features are prominently visible in the deformed ice-templated composite. Within the kink band, all the walls well maintained straightness. At the boundary regions of the band, epoxy walls experienced severe plastic deformation and underwent significant rotation. The severe fracture occurred within the Al$_2$O$_3$ walls, which is expected due to the brittle nature of Al$_2$O$_3$. Thus, during the rotation of the epoxy walls in the boundary areas of the kink band through plastic deformation, each Al$_2$O$_3$ wall experienced brittle fracture at numerous locations to keep up with the rotation of the adjacent epoxy walls. Nevertheless, the boundary regions of the kink band are observed to be less damaged compared to that on the exterior surface, where crack propagation across the interfaces caused clear separation in the material. Unlike the interior region, epoxy walls at the exterior surface did not experience significant rotation but fractured similar to the Al$_2$O$_3$ walls.
From the SEM image in Figure 93a, the distribution of the orientation of the walls was determined for three regions: outside the kink band (region A), the boundary of the kink band (region B), and the middle of the kink band (region C). Yellow dashed boxes indicate these three regions in Figure 93a, and the orientation distributions are presented in Figure 93b. The method to determine the orientation distribution is as follows. SEM images of the deformed composite specimen were analyzed using Fiji (NIH, USA) image processing software package. First, the SEM images were corrected for brightness and contrast. Next, a segmentation step was performed to binarize an SEM image into bright (ceramic lamella wall) and dark (epoxy phase) regions. Along the growth direction of ice crystals, fast Fourier transform (FFT) analysis was performed over the oriented ceramic lamella walls using the Directionality plugin (http://fiji.sc/wiki/index.php/Directionality). The plugin provides the distributions within the user-defined range of angular orientations and generates a Gaussian fit to the FFT signal. The analysis for the orientation distribution for three regions shown in Figure 93a (A, B, C) was performed individually, and the corresponding Gaussian fits are shown in Figure 93b.
Figure 85: (a) SEM image revealing kink band, $\theta = 0^\circ$, and (b) orientation distributions of the walls corresponding to the regions A, B and C indicated in (a).

The orientation distribution for region A represents the misalignment of lamella walls in the fabricated materials, i.e., prior to deformation. For region A, most of the walls are observed to be tilted by a few degrees relative to the reference vertical dashed gray line, and the average tilt angle ($\theta$) is $2.5^\circ$. This is expected since, in ice-templated ceramics, not all the lamella walls develop precisely parallel to the direction of an applied temperature gradient, and the walls are also not perfectly parallel to each other [166,172]. For region B, the orientation distribution has widened significantly, which is because region B contains walls both outside and inside of the kink band. The orientation distribution also shifted significantly relative to region A. $\theta$ for region B is $8.5^\circ$. For region C, the orientation distribution is similar to that of region A (narrow) but shifted further, and $\theta$ is $17.4^\circ$. While a large region tilted significantly due to the kink band formation, the comparable orientation distribution between regions A and C suggests minor deformation in the interior of the kink band.

Unidirectional fiber-reinforced polymer composites or laminates typically contain regions of misaligned fibers. As a result, a misalignment exists between the fibers and compression direction, which plays a critical role in triggering the kink bands [178,180]. The critical compressive stress of composite ($\sigma_c$) at the initiation of kink band is influenced by the initial fiber misalignment ($\phi_o$) and shear yield strength of composite ($\tau_y$) as [180–182]:

$$\sigma_c = \frac{\tau_y}{\phi_o}.$$

(1)
Both lower \( \tau_y \) and greater \( \phi_o \) favor kink band development and thus reduce the compressive strength of composites. During the uniaxial compression with the loading direction aligned with the fibers, within a region or band of the material containing the slightly misoriented fibers, the misalignment induces bending of the fibers. Also, a resolved shear stress is induced in the direction of misaligned fibers, leading to yielding of the polymer matrix phase by reaching the shear yield stress of the matrix [182]. Argon [181] suggested that \( \sigma_c \) is reduced further by the additional fiber rotation angle (\( \phi \)) within the kink band as:

\[
\sigma_c = \frac{\tau_y \phi_o}{\phi_o + \phi}. \tag{2}
\]

Due to the constraint imposed by the surrounding material, the shear induces a rotation and increases the resolved shear stress in the misoriented region. The resultant geometric softening by the shear deformation and rotation creates a localized band of misoriented material, i.e., kink band [178,180]. As the matrix phase yields, particularly at the boundary of the kink band, the lateral mechanical support by the matrix phase to the fibers becomes inadequate, and the composite becomes unstable. Depending on the fiber type (brittle or flexible), the fibers will either break or rotate [177]. Similarly, the orientation misalignment between the ceramic walls in ice-templated composite and the compressive loading direction might have also resulted in the yielding of the epoxy matrix and triggered kink band formation (plastic micro-buckling).

Investigation of the loading surfaces (top and bottom, perpendicular to the growth direction of ice crystals) revealed the presence of several large tortuous cracks. The SEM image in Figure 94a shows one of those large tortuous cracks on the top surface. The observed large cracks indicate longitudinal splitting in the composite, where the cracks most likely originated on the loading surfaces. The higher magnification SEM images in Figures 94b-e reveal the various characteristics of crack propagation, such as crack propagation perpendicular to \( \text{Al}_2\text{O}_3 \)-epoxy interface (Figure
94b), crack propagation along the domain boundary (Figure 94c), crack deflection at the domain boundary (Figure 94d), and crack propagation parallel to Al$_2$O$_3$–epoxy interface, delamination (Figure 94e). Ice-templated Al$_2$O$_3$–epoxy composites consist of numerous domains that are perpendicular to the growth direction of ice crystals. Each domain consists of parallel layers of Al$_2$O$_3$ and epoxy, and the layer orientation changes from one domain to another. Thus, the domains are randomly oriented on a plane (e.g., loading surface) perpendicular to the growth direction of ice crystals. On a surface perpendicular to the growth direction of ice crystals, a crack can only propagate a distance along the interface or domain boundary before it encounters an obstacle due to the presence of multiple domains, which would force the crack to change the orientation. If the resistance exerted by the obstacle at the crack tip is too high, the crack will be unable to propagate further, or the crack will change the orientation and continue to propagate along another interface or domain boundary of a different orientation. The crack can also be forced to propagate through the layers. Thus, due to multiple domains, as the crack path continuously changes the orientation (attributing crack path tortuosity), ice-templated hierarchical microstructure provides an inherent resistance to crack propagation and increases the fracture surface area. Next, the material was removed from the top surface using the procedure described in Section 2.2, and Figure 94f reveals the deformation characteristics on the interior surface, which are similar to that observed on the top surface. Note that the region observed in Figure 94f is not directly beneath the region observed in Figure 94a.
Figure 86: (a) Tortuous crack path on the loading surface for $\theta = 0^\circ$. Higher magnification SEM images revealing the characteristics of crack propagation: (b) crack propagation perpendicular to interface, (c) crack propagation along domain boundary, (d) crack deflection at domain boundary, and (e) crack propagation parallel to interface. (f) Similar deformation features on the interior surface (after 1 mm material removal from the top loading surface). Note that the region observed in Figure 94f is not directly below the region observed in Figure 94a.
Figure 95 shows a reconstructed nano-CT 3D volume rendering of a damaged specimen extracted from a deformed composite sample (see schematic in Fig. 90d), for the loading orientation of $\theta = 0^\circ$. Note that Figure 95 represents a region that is almost in the middle of the deformed composite specimen. Figure 95 shows longitudinal cracks on the top surface (x-y plane) and kink band on the y-z plane. The crack observed at an angle to the loading direction on the x-z plane and y-z plane is present at the boundary of the kink band. The wide dark regions correspond to the regions of severe damage and most likely resulted from longitudinal splitting and due to the interactions between kink band and longitudinal cracks (discussed in the next paragraph); however, not necessarily that the material was completely separated in those regions. It is likely that the size of the ceramic wall fragments present within the wide dark regions were well below the spatial resolution of measurement and hence are not visible in the X-ray tomograph.
**Figure 87:** A reconstructed nano-CT 3D volume rendering of a specimen extracted from a deformed composite specimen (see schematic in Figure 90d), $\theta = 0^\circ$. Loading and growth directions are along the $z$-direction.
Figure 88: (a) A reconstructed nano-CT 3D volume rendering in which x-y and y-z planes are mainly visible. (b) X-ray tomographs of y-z plane at the back and x-y plane at the bottom. Rest of
the images (c-l) reveal damage evolution on y-z plane at different distances along x-direction (starting from back) and on x-y plane at a fixed height (420 µm) along z-direction. Yellow dashed line indicates the intersection between x-y plane and y-z plane.

For further insights into the damage characteristics, different regions within the reconstructed volume are shown in Figure 96. In the 3D volume rendering in Figure 96a, x-y and y-z planes are mainly observed. Figure 96b reveals an X-ray tomograph of the y-z plane at the back and the x-y plane at the bottom within the reconstructed volume. Comparing the top and bottom planes suggests severe damage through longitudinal cracking in the bottom part of the specimen. The rest of the images (Figures 96c-l) allow visualizing the damage evolution on the y-z plane at different distances along the x-direction starting from the back (left column) and on the x-y plane at a fixed height along the z-direction (right column). These images reveal that kink band is present throughout the volume (1190 µm × 810 µm × 840 µm) and suggest that the deformation band mostly likely developed over a greater volume within the tested specimen (6 mm × 6 mm × 3 mm). Significant damage occurred within the deformation band, and it appears that the kink band formed first, followed by a fracture within the band. The severe damage within the kink band regions originated from the interactions of the band with the longitudinal cracks, which is more clearly evident from the images in the right column. The longitudinal cracks most likely originated on the loading surfaces and propagated along the loading direction. Note that although the compression test was stopped as soon as maximum stress was reached, significant damage already occurred in the material. Thus, both damage forms evolved in the vicinity of peak stress; however, it was difficult to predict whether both failure mechanisms developed simultaneously or one developed before the other. Nevertheless, Figure 96 strongly indicates that as the longitudinal
cracks propagated through the specimen, they interacted with the kink band and caused severe material damage.

The above investigations thus revealed that for the loading orientation of $\theta = 0^\circ$, kink band formation and longitudinal splitting are the two dominant deformation mechanisms that triggered a failure in the composite. Kink band developed at an angle to the loading direction, whereas longitudinal cracks formed along the loading direction. In this work, compression tests were stopped in the vicinity of peak stress (~700 MPa). Our previous study revealed that the composite specimens that exhibited strength in the range of 700 MPa also failed catastrophically [172]. While it is challenging to ascertain which mechanism or if a combination of the mechanisms triggered the catastrophic failure in ice-templated Al$_2$O$_3$–epoxy composites, the formation and propagation of kink band have been attributed as responsible for catastrophic failure in unidirectional fiber-reinforced composites under compression [180,182,183]. Therefore, similarly, kink band initiation and propagation itself could be responsible for triggering the catastrophic-type failure in ice-templated Al$_2$O$_3$–epoxy composites.

**8.3.3 Deformation mechanisms for compression direction of $\theta = 45^\circ$ and $\theta = 90^\circ$**

The SEM images in Figure 97 reveal the damage characteristics for the loading orientation of $\theta = 45^\circ$. The inset in Figure 97a shows a simple schematic illustrating the orientation of the ceramic walls relative to the loading direction. On the side surface (Figure 97a), which shows the walls oriented along the growth direction of ice crystals, delamination (indicated by yellow arrows) at the Al$_2$O$_3$–epoxy interfaces is observed to be the dominant failure mechanism. A higher magnification image of the interface delamination is shown in Figure 97b. Since the walls are oriented approximately 45° to the loading direction, the resolved shear stress from the applied uniaxial compressive load is expected to cause delamination along the interfaces. Cracks can also
be seen (indicated by orange arrows), which propagated across the interfaces, Figure 97c. The SEM image in Figure 97d shows one of the loading surfaces, which reveals crack propagation mainly along the Al₂O₃–epoxy interfaces, thus interface delamination. Figure 98a shows a reconstructed nano-CT 3D volume rendering of a damaged specimen extracted from a deformed composite sample. The images in Figure 98b-d reveal damage on the y-z plane at different distances along the x-direction and thus enable to visualize damage in the interior regions of the specimen. Figure 98 also reveals delamination in the deformed specimen and further shows fracture within ceramic walls and suggests significantly less damage in the composite than that for the loading orientation of $\theta = 0^\circ$. 
**Figure 89:** (a) SEM image of the side surface revealing inelastic deformation features of a partially deformed specimen, $\theta = 45^\circ$. (b, c) Higher magnification SEM images of some of the deformation features observed in (a). Yellow arrows point to the delamination cracks along Al$_2$O$_3$–epoxy interfaces, whereas orange arrows point to the cracks propagated across the interfaces. (d) Higher magnification SEM image revealing interface delamination on the loading surface.
Figure 90: (a) A reconstructed nano-CT 3D volume rendering of a specimen extracted from a deformed composite specimen (see schematic in Figure 90d), $\theta = 45^\circ$. Loading direction is along the z-direction. Rest of the images (b-d) reveal damage evolution on y-z plane at different distances along x-direction (starting from back). Yellow dashed line indicates the intersection between x-y plane and y-z plane.
**Figure 91:** (a) SEM image of the side surface revealing inelastic deformation features of a partially deformed specimen, $\theta = 90^\circ$. (b, c) Higher magnification SEM images of some of the deformation features observed in (a). Yellow arrows point to the delamination cracks along Al$_2$O$_3$–epoxy interfaces, whereas orange arrows point to the cracks propagated across the interfaces. (d) Higher magnification SEM image revealing interface delamination on the loading surface.
Figure 92: (a) A reconstructed nano-CT 3D volume rendering of a specimen extracted from a deformed composite specimen (see schematic in Figure 90d), $\theta = 90^\circ$. Loading direction and growth direction are along the z-direction and x-direction, respectively. Rest of the images (b-d) reveal damage evolution on x-z plane at different distances along y-direction (starting from back). Yellow dashed line indicates the intersection between x-y plane and x-z plane.

The damage characteristics on the surfaces of the deformed sample for $\theta = 90^\circ$ are shown in Figure 99. The inset in Figure 99a shows a simple schematic illustrating the orientation of the ceramic walls relative to the loading direction. On the side surface (Figure 99a), cracks developed both along the $\text{Al}_2\text{O}_3$–epoxy interfaces (i.e., delamination) and across the interfaces, which can be
further observed in the higher magnification SEM images (Figures 99b and 99c). It is suggested that during compression, as the layers slide past each other due to shear, cracks developed on the side surface. On the loading surface (Figure 99d), delamination along the Al$_2$O$_3$–epoxy interfaces can be observed. Figure 100a shows a reconstructed nano-CT 3D volume rendering of a damaged specimen, which was extracted from a deformed composite sample for further insights. The images in Figures 100b-d reveal damage on the x-z plane at different distances along the y-direction. Figure 100a shows that significant delamination occurred in the interior of the specimen. A large delamination crack on the y-z surface is observed to be approximately 45° relative to the loading direction, which further confirms that delamination is the dominant failure mechanism. Additionally, Figures 100b-d reveal cracks within the ceramic walls, and that propagated across the interfaces.

**Figure 93:** Brittle cracks within ceramic lamella walls for (a) $\theta = 45^\circ$ and (b) $\theta = 90^\circ$. Here, the cracks are represented in red color.
Thus, for both $\theta = 45^\circ$ and $\theta = 90^\circ$, interface delamination and fracture within the lamella walls and across the $\text{Al}_2\text{O}_3$–epoxy interfaces are observed to be the main inelastic deformation mechanisms, which triggered a macroscopic failure in the composite. The current results further revealed that the deformation mechanisms that caused the failure in the ice-templated composites for the loading orientations of $\theta = 45^\circ$ and $\theta = 90^\circ$ are significantly different from the failure mechanisms evolved at $\theta = 0^\circ$. The cracks developed within the ceramic walls for the loading orientations of $\theta = 45^\circ$ and $\theta = 90^\circ$ are shown in Figure 101. Here, the cracks are represented in red color, and the methodology is discussed in Section 2.2. It can be seen that for both loading orientations, the lamella wall cracks are distributed over the entire volume, which suggests the delocalized nature of brittle fracture in the composite. For the loading orientations of $\theta = 45^\circ$ and $\theta = 90^\circ$, it is possible that interface delamination and fracture within the lamella walls could be the compressive strength limiting factors. However, these damage mechanisms did not cause catastrophic failure, and hence the materials exhibited progressive-type failure response [172]. With the continuation of uniaxial compression, interface delamination, fracture within the ceramic walls, and the yielding of epoxy evolve in a progressive manner, attributing the ductile-like macroscopic compressive failure response. This is consistent with that the overall level of damage in the recovered specimens for $\theta = 45^\circ$ and $\theta = 90^\circ$ was significantly less than that for $\theta = 0^\circ$. At both $\theta = 45^\circ$ and $\theta = 90^\circ$, ice-templated composite experienced a significant reduction in compressive strength due to the strong influence of the weak, ductile epoxy phase on the compressive response. The progressive deformation regime is mainly dominated by the plastic flow of epoxy and the continued interface delamination and fracture within ceramic walls.
8.4 Discussion

The current results revealed that similar to the compressive strength, the inelastic deformation mechanisms which trigger failure in ice-templated composites are also strongly dependent on the loading direction (relative to the layer orientation). Figure 102 shows a schematic depicting the variation of compressive strength of ice-templated Al₂O₃–epoxy composites with the loading orientation (θ) and mentions the deformation mechanisms at different θ. In Figure 102, the yellow shaded region is shown, based on the prior study by Akurati et al. [172], to indicate that at each θ, composites exhibited a large scatter in the strength values. This work also provides significant insights into the strength–deformation mechanism relationships for the different directions of compressive loading relative to layer orientation.

In ice-templated porous ceramics, the primary structural component is the tall, slender lamella walls. For the compressive loading direction of θ = 0°, lamella walls (hard phase) carry the applied load [29,55,77,79,184]. The load-bearing capacity of ice-templated porous ceramics has been suggested to strongly depend on the resistance of the lamella walls to elastic instability, i.e., buckling, which is characterized by a sudden sideways failure of a structural member subjected to uniaxial compressive stress [29,55,79,184,185]. Lamellar bridges between the adjacent lamella walls anchor the walls and provide structural, mechanical stability to ice-templated ceramics [29,55,77,79,184]. However, ice-templated ceramics fabricated from low solid loading suspensions exhibit a negligible density of bridges and low strength [29,55,77,79,184]. Recall that the ice-templated sintered Al₂O₃ materials fabricated from 20 vol.% solid loading suspensions exhibited lamellar morphology with a negligible density of lamellar bridges (Figure 90e), and the uniaxial compressive strength of these materials was below 20 MPa [172].
On the other hand, the infiltrated ice-templated composites exhibited a significant increase in the uniaxial compressive strength compared to the porous ceramics. According to the Tsai-Hill failure criterion, strength ($\sigma_p$) of an orthotropic composite at an arbitrary angle $\theta$ relative to the loading direction can be estimated as [11,49,146,172]:

$$
\frac{1}{\sigma_p^2} = \frac{1}{\sigma_L^2} (\cos^4 \theta - \sin^2 \theta \cos^2 \theta) + \frac{1}{\tau_s^2} (\sin^2 \theta \cos^2 \theta) + \frac{1}{\sigma_{T}^2} (\sin^4 \theta).
$$

(3)

$\sigma_L$ is the longitudinal strength ($\theta = 0^\circ$), $\sigma_T$ is the transverse strength ($\theta = 90^\circ$), and $\tau_s$ is the in-plane shear strength of the composite. Using the equal-strain Voigt hypothesis (i.e., the rule of mixture), $\sigma_L$ can be estimated as [17,24,25,45]:

$$
\sigma_L = \sigma_{\text{epoxy}} V_{\text{epoxy}} + \sigma_{\text{Al}_2\text{O}_3} V_{\text{Al}_2\text{O}_3},
$$

(4)

where $\sigma_{\text{epoxy}}$ is the yield strength of bulk epoxy and $\sigma_{\text{Al}_2\text{O}_3}$ is the fracture strength of bulk $\text{Al}_2\text{O}_3$. Similarly, $V_{\text{epoxy}}$ and $V_{\text{Al}_2\text{O}_3}$ are the volume fractions of epoxy and $\text{Al}_2\text{O}_3$ phases, respectively, in the composite. At $\theta = 0^\circ$, $\sigma_p = \sigma_L$. The yield strength of epoxy is about 87 MPa only [172]. The previous study showed that the compressive strength values of ice-templated $\text{Al}_2\text{O}_3$–epoxy composites (of the same composition used in this study) for the loading direction of $\theta = 0^\circ$ reside within a wide range of 380–684 MPa [172]. Therefore, $\sigma_L$ (strength of ice-templated composites at $\theta = 0^\circ$) is strongly governed by $\sigma_{\text{Al}_2\text{O}_3}$ or, more specifically, by the failure resistance of ceramic lamella walls. In the composite, at $\theta = 0^\circ$, ceramic walls are the main load-bearing elements [11]. In the absence of epoxy layers, tall, slender ceramic walls are too weak to sustain any appreciable compressive load [172]. On the other hand, in the composite, the epoxy layers provide rigid mechanical support to the ceramic walls, allowing the walls to carry a remarkably greater compressive load and hence the drastic increase in strength.

Naleway et al. [49] investigated the uniaxial compressive response of ice-templated zirconia ($\text{ZrO}_2$)–epoxy composites for the loading direction of $\theta = 0^\circ$. This study did not perform
any microstructural investigation of deformation mechanisms. However, they suggested that the polymer layers provide rigid mechanical support to the ceramic walls and prevent the walls from undergoing premature compressive failure by Euler buckling [180]. Naleway et al. [49] also performed a theoretical analysis to characterize the compressive mechanical behavior of the composites, in which the Euler buckling mode of failure in ZrO₂ walls was considered as the strength limiting mechanism. The current work revealed kink band formation (plastic micro-buckling) in ice-templated composites for the loading direction of θ = 0⁰, which can be assumed to be the strength limiting failure mechanism. As discussed in Section 3.2, in ice-templated ceramic-polymer composites, the kink band formation results from the inherent misalignment of the Al₂O₃ walls and the plastic shear deformation of the epoxy matrix phase during compressive deformation, which also resulted in a severe fracture of ceramic walls and catastrophic failure. The observed failure mechanisms in ice-templated Al₂O₃–epoxy composites at θ = 0⁰ are different from those reported for ice-templated Al₂O₃–Al-12Si (ceramic–metal) composite for which microstructural analysis did not reveal any trace of kink band formation [166]. Thus, the current study provides some of the first evidence and insights of failure by kink band formation in ice-templated ceramic–polymer composites.

The knowledge of the failure mechanisms for the loading direction θ = 0⁰ further helps to interpret the compressive strength data of ice-templated Al₂O₃–epoxy composites. According to Akurati et al. [172], for θ = 0⁰, the measured strength values were observed to be in the range of 380–684 MPa. Using 684 MPa and 380 MPa as the maximum and minimum σₚ, from equation (4), the maximum and minimum σ_{Al₂O₃} values are obtained as 2.1 GPa and 1.1 GPa, respectively. Considering that σ_{Al₂O₃} represents the crushing strength of ceramic walls in the composite, it can be stated that all the ceramic walls do not fail at a single crushing strength value. Interestingly, the
maximum and minimum $\sigma_{\text{Al}_2\text{O}_3}$ values fall in between the uniaxial compressive strength (2.5 GPa) [148] and flexural strength (510 MPa) [163] of bulk $\text{Al}_2\text{O}_3$. Thus, it can be interpreted that the ceramic walls neither fail in pure compression mode of failure nor pure bending mode of failure. The interpretation well follows the results of this study, which revealed kink-band formation (micro-plastic buckling) in the composite. While it is expected that the yield strength of epoxy remains the same across the samples, the resolved shear stress in the epoxy matrix can change with the variation of the compressive load-bearing capacity of ceramic walls (thus the strength of ceramic walls). The higher the load-bearing capacity of the ceramic walls, the lower the resulting resolved shear stress in the epoxy matrix; hence the macroscopic compressive stress (i.e., the strength of composite) will increase before failure initiation by kink band formation. Roy et al. [166] suggested that the variability in the compressive strength of ceramic walls (i.e., load-bearing capacity) in ice-templated composites is related to the inherent defects in the walls. However, it is also possible that the inherent misalignment of ceramic walls varies from specimen to specimen and attributes to the variability of the load-bearing capacity of the walls.

For the loading directions of $\theta = 45^\circ$ and $\theta = 90^\circ$, failure by delamination at the $\text{Al}_2\text{O}_3$–epoxy interfaces (about $45^\circ$ to loading direction) was influenced by the resolved shear stress and prompted by the weak interfacial shear strength. It has been reported that in ice-templated ceramic–polymer composites, interfaces are inert and hence weak [47]. While ice-templated $\text{Al}_2\text{O}_3$–epoxy composites exhibited decreased compressive strength with $\theta$, the strength reduction was observed to be drastic in the range of $\theta = 0–15^\circ$ [172]. Whereas, in the range of $\theta = 15–90^\circ$, composites exhibited a gradual decrease of strength with $\theta$. Also, ice-templated composites showed a tendency to fail catastrophically (brittle-like failure) for loading direction along and close to the growth direction of ice crystals, but progressive-type (ductile-like) failure away from the growth direction.
Away from the growth direction of ice crystals, contribution of the epoxy phase to compressive response increases, which decreases strength but attributes ductile-like response to composites [11,172]. The current results suggest that the abrupt change in compressive strength and macroscopic failure behavior of ice-templated ceramic–polymer composites with θ (within a narrow range) is directly related to the changes in the inelastic deformation mechanism. Along and close to the growth direction of ice crystals, compressive strength is dominated by the load-bearing contribution of ceramic walls. However, failure is triggered by the yielding of the matrix (plastic micro-buckling) and subsequent fracture of the walls. With the increasing θ, other mechanisms kick in (interface delamination, fracture in ceramic walls, and yielding of epoxy), which significantly weaken the composites and drastically reduce the compressive strength.

**Figure 94**: A schematic depicting the variation of compressive strength of ice-templated Al₂O₃–epoxy composites with the loading orientation (θ). Also, mentioned are the deformation
mechanisms at different $\theta$. The yellow shaded region is shown, based on our prior study [172], to indicate that at each $\theta$, composites exhibited a large scatter in the strength values.

Finally, a comparison of uniaxial compressive response and failure mechanisms is made between ice-templated $\text{Al}_2\text{O}_3$–epoxy composite and nacre (develops in the inner layers of red abalone shell), a widely investigated natural biocomposite [2,8,15,41,186,187], for different loading directions. However, it is important to note the differences in composition and microstructure between ice-templated composites and nacre. In the ice-templated $\text{Al}_2\text{O}_3$–epoxy composite investigated in this work, ceramic content is only about 30 vol.%, whereas nacre contains 95 vol.% calcium carbonate (CaCO$_3$), a ceramic phase. Ice-templated composites have a multilayered architecture, whereas nacre exhibits a brick-and-mortar type architecture. Nacre is mainly composed of CaCO$_3$ polygonal-shaped platelets, where the platelets are about 5-8 $\mu$m in diameter and 200-900 nm in thickness [2,15,41]. The CaCO$_3$ platelets are bonded together by an organic phase of 10-50 nm thickness, resulting in a brick-and-mortar structure [2,15,41]. Nevertheless, the comparison is relevant since the uniaxial compressive strength and failure mechanism in nacre also depend strongly on the loading direction relative to layer orientation [8,15,186,187].

According to Menig et al. [8], the uniaxial compressive strength of abalone shell in the loading direction perpendicular to layers ($\theta = 90^\circ$) was found to be in the range of 450 – 700 MPa, whereas only about 200 MPa for the loading direction parallel to layers ($\theta = 0^\circ$). In another study, Jiao et al. [187] investigated the off-axis uniaxial compressive response of nacre for various loading directions in the range of $\theta = 0^\circ$–90$^\circ$. This study reported a gradual decrease in strength with the increasing $\theta$ from $0^\circ$ to $45^\circ$, whereas a significant increase in strength with $\theta$ from $45^\circ$ to $90^\circ$. Also, the study revealed that the uniaxial compressive strength of nacre at $\theta = 90^\circ$ is
considerably higher than that at $\theta = 0^\circ$. While the $\theta$-dependence of compressive strength of ice-templated composites is similar to that of nacre, the major difference is that the former material exhibits the highest strength for loading direction parallel to the layers ($\theta = 0^\circ$), whereas in the latter material strength is highest for the loading direction perpendicular to the layers ($\theta = 90^\circ$). Also, for ice-templated composites, compressive strength decreases drastically between $\theta = 0^\circ$–$20^\circ$, but beyond that strength decrease is only moderate [172]. Another difference is in failure strain. In nacre, failure strain is higher in the direction along which strength is also higher ($\theta = 90^\circ$). In contrast, in ice-templated composites, failure strain is the lowest at $\theta = 0^\circ$, where strength is the highest, compared to other loading directions (Figure 90g).

For uniaxial compressive loading direction parallel to layers, nacre also exhibits axial splitting and kink band formation caused by plastic microbuckling [8,186,187]. Thus, both nacre and ice-templated composite exhibit kink band formation for compression direction parallel to layers. However, in ice-templated composite, this mechanism occurs in the direction where the material exhibits the highest compressive strength, which is not the case in nacre. For compression direction perpendicular to layers, nacre exhibits crack deflection at ceramic–polymer interfaces, as well as crack propagated along interfaces [8]. The weaker organic phase (viscoelastic layers) also allowed sliding of CaCO$_3$ platelets to incorporate larger deformation. In the intermediate loading orientations, inter-lamellar shearing and trans-platelet fragmentation have been reported [187].

8.5 Conclusions

This work reveals that the inelastic deformation mechanisms, which trigger failure in ice-templated ceramic–polymer composites, are strongly influenced by the uniaxial compressive loading direction relative to the growth direction of ice crystals (i.e., layer orientation). Since the
uniaxial compressive strength is also strongly influenced by the loading direction, this study sheds important insights into the strength–deformation mechanism relationships in ice-templated ceramic–polymer composites.

For the loading direction parallel to the growth direction \((\theta = 0^\circ)\), kink band formation (plastic micro-buckling) and longitudinal splitting were observed to be the main inelastic deformation mechanisms. The current study provides some of the first evidence of failure by kink band formation in ice-templated ceramic–polymer composites. For the loading direction of \(\theta = 0^\circ\), ceramic walls are the main compressive load-bearing elements and enhance the strength of composites compared to other loading directions. It is possible that kink band formation, which results from the shearing instability of the soft matrix phase, could be the primary strength limiting factor and responsible for the observed catastrophic-type compressive failure response.

For the loading directions of \(\theta = 45^\circ\) and \(\theta = 90^\circ\), interface delamination and fracture within the lamella walls and across the Al₂O₃–epoxy interfaces were the main inelastic deformation mechanisms. Thus, away from the growth direction of ice crystals, other mechanisms kick in, which significantly weaken the composites and drastically reduce the compressive strength but attribute progressive-type failure to ice-templated ceramic–polymer composites. The current results are vital to improving further the understanding of structure–mechanical property relationships in hierarchical ice-templated composites and designing these hierarchical materials with the targeted properties.

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CHAPTER 9

SUMMARY AND CONCLUSIONS

The purpose of this dissertation is many-folds with a central theme of tunable compressive response, which has been revealed by investigating microstructure-mechanical property relationships in both ice-templated ceramics and infiltrated composites.

First, AC electric fields were employed to explore the interactions of aqueous ceramic suspensions with applied field duration, frequency, and voltage. Field application to an aqueous ceramic suspension resulted in a net motion of ceramic particles due to DC voltage generation. Further, suspension concentration increased near one of the electrodes, controllable through AC frequency and field duration. Exploratory research on the DC voltage generation factors deriving empirical relations to estimate mass accumulation. For a given concentration of dispersant, electrical conductivity can be estimated. Thus, the amount of mass accumulated can be predicted. This work was essential in understanding the influence of the AC field and how it can exploit to vary the local concentration.

Further, the influence of the local concentration on the ice-templating process was investigated to fabricate porous ceramics with changing field duration density of the very bottommost regions in sintered materials increased and attributed to increased local suspension concentration. The templated microstructure turned increasingly dendritic with field duration, suggesting a strong influence of local concentration on the growth characteristics of ice crystals. The AC-field assisted materials exhibited enhanced compressive strength. Most importantly, for a negligible change in porosity. This work contributes to advancing the ice-templating technology using externally energized fields.
Secondly, ice-templated porous ceramics were fabricated using a conventional ice-templating process [19]. Investigations were performed to evaluate the role of microstructure on the mechanical properties (quasistatic and dynamic loads) and mechanical performance (sphere impact). The microstructure was systematically varied as an FFV and solid loading function to understand the strain rate dependence on mechanical behavior. Under quasistatic loading, the origin of progressive crushing type failure was observed. After peak stress, damage evolved only in minimal fragmentation, which gradually increased with the strain. The damage in the dynamic regime was relatively less than that in the quasistatic regime, suggesting enhanced resistance to brittle fracture at high-strain rates. This study revealed ice-templated porous materials possess more excellent structural stability at high-strain rate compressive loads.

Further, sphere impact response revealed a strong influence of the templated microstructure. With a finer microstructure (fabricated at high FFV), the impact resistance of the materials increased, and the radius of the damage crater, depth-of-penetration, and mass loss decreased. The impact process evolved in three phases; penetration, dwell and rebound. The final templated microstructure affected the impact resistance and the duration of these phases.

Finally, this dissertation explores the fabrication of ice-templated ceramic-polymer composites. With low pore tortuosity, the infiltration of the polymer phase was performed at ease. The resulted materials resembled bioinspired multilayered composites. This works explored the role of solid loading, layer connectivity, pore morphology on the compressive mechanical behavior. Under high-strain rate loading, ice-templated composites exhibited strain rate sensitivity, with enhanced mechanical properties under dynamic loads. Further, in a quest to fabricate materials with structural gradient observed in most natural materials. This work takes the pivotal step to characterize the role of loading direction relative to layer orientation under compressive
loads. Ice-templated alumina-epoxy composites were employed as a model system for this endeavor. It is to be noted that this investigation is not on the development of multilayered composites with a structural gradient. However, the current results can help understand mechanical behavior and the design of materials with structural gradients. For compression along the growth direction of ice crystals, specimens exhibited either high strength with brittle-like (catastrophic) failure or low strength with ductile-like (progressive) failure. Away from growth direction, strength decreased significantly, and failure was ductile-type. The strength exhibited a strong dependence on ceramic fraction and morphology. At each orientation, strength data of both porous ceramics and composites showed significant variability, and Weibull analysis suggested a connection between their strength. Towards the end, the inelastic deformation mechanisms in ice-templated alumina–epoxy composites were also investigated for the loading directions of 0-degree (parallel to the growth direction), 45-degree (to the growth direction), and 90-degree (to the growth direction). This study made the first attempt to reveal the underlying inelastic deformation mechanisms in ice-templated ceramic–polymer composites under compressive loading—an essential step towards understanding structure–mechanical property relationships, and hierarchical materials design.

To this end, the work performed in this dissertation provides a fundamental understanding of microstructure mechanical property correlations. It establishes design guidelines to fabricate ice-templated materials for tunable mechanical behavior properties for targeted structural and impact energy absorption applications.
REFERENCES


[32] I. Nelson, L. Gardner, K. Carlson, S.E. Naleway, Freeze casting of iron oxide subject to a


[55] M. Banda, D. Ghosh, Effects of porosity and strain rate on the uniaxial compressive


[85] R. Beiranvand, Analyzing the uniformity of the generated magnetic field by a practical one-


https://doi.org/10.1016/j.jeurceramsoc.2015.10.018.


[144] S. Deville, S. Meille, J. Seuba, A meta-analysis of the mechanical properties of ice-


https://doi.org/10.1007/S10853-010-4683-1.


[168] D. Raabe, A. Al-Sawalmih, S.B. Yi, H. Fabritius, Preferred crystallographic texture of α-


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VITA

Sashanka Akurati received his Bachelor of Technology (B. Tech) degree in Mechanical Engineering from Karunya Institute of Technology and Sciences, India, formerly Karunya University, in 2014. Later he completed his Master of Technology (M. Tech) degree specializing in Materials Technology from National Institute of Technology Warangal (NITW), India, in 2016. Between 2015-16, he worked as a Project Trainee at Bhabha Atomic Research Centre (BARC), India. At BARC, his research project was on the scratch and indentation behavior of dense boron carbide (B₄C) ceramics. Upon graduating from NITW, he further pursued higher education for his Ph.D. in the Mechanical & Aerospace Engineering department at Old Dominion University, under the supervision of Dr. Dipankar Ghosh. During this period, he conducted research on processing and mechanical characterization of ice-templated porous ceramics & ceramic-polymer composites. His research developed a novel methodology to employ an alternating current (AC) electric field to fabricate ice-templated ceramics. Mr. Sashanka Akurati completed his Ph.D. dissertation in 2021.