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Complex Composites Built Through Freezing

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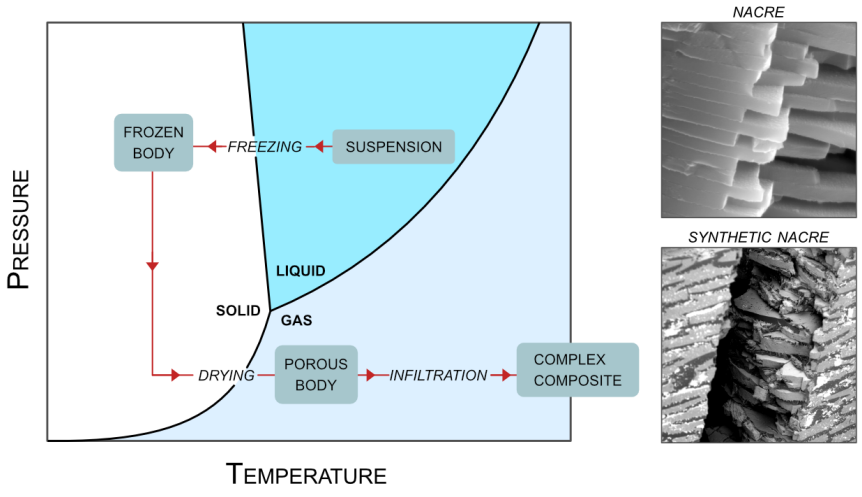
CONSPECTUS: Using a limited selection of ordinary components and at ambient temperature, nature has managed to produce a wide range of incredibly diverse materials with astonishingly elegant and complex architectures. Probably the most famous example is nacre, or mother-of-pearl, the inner lining of the shells of abalone and certain other mollusks. Nacre is 95 percent aragonite, a hard but brittle calcium carbonate mineral, that exhibits fracture toughness exceedingly greater than pure aragonite, when tested in the direction perpendicular to the platelets. No man-made composite outperforms its constituent materials by such a wide margin. Nature's unique ability to combine the desirable properties of components into a material that performs significantly better than the sum of its parts has sparked strong interest in bioinspired materials design.

Inspired by this complex, hierarchical architecture, many processing routes have been proposed to replicate one or several of these features. New processing techniques point to a number of laboratory successes that hold promise in mimicking nacre. We pioneered one of them, ice-templating, in 2006. When a suspension of particles is frozen, particles are rejected by the growing ice crystals and concentrate in the spacing in between the crystals. After the ice is freeze-dried, the resulting scaffold is a porous body that can eventually be pressed to increase density and then be infiltrated with a second phase, providing multi-layered, lamellar complex composites with a microstructure reminiscent of nacre. The composites exhibit a marked crack deflection during

crack propagation, enhancing the damage resistance of the materials, offering an interesting trade-off of strength and toughness.

Freezing as a path to build complex composites has turned out to be a rich line of research and development. Understanding and controlling the freezing routes and associated phenomena has become a multidisciplinary endeavor. A step forward in the complexity was achieved with the use of anisotropic particles. The ice-induced segregation and alignment of platelets can yield dense, inorganic composites (nacre-like alumina) with a complex architecture and microstructure, replicating several of the morphological features of nacre. Now, a different class of complex composites is quickly arising: engineered living materials, developed in the soft matter and biology communities. The material-agnostic nature of the freezing routes, combined with the use of an aqueous system, the absence of organic solvents, and the low temperatures being used, are all strong assets for the development of such complex composites. More complex building blocks, such as cells or bacteria, can be frozen. Understanding the fundamental mechanisms controlling the interactions between the ice crystals and the objects, as well as the interactions between the soft objects themselves and ther fate, are essential in this context.

In this Account, we highlight our efforts over the past decade to achieve controlled synthesis of nacre-like composites and understand the associated processes and properties. We describe the unique hierarchical and chemical structure of nacre, and the fabrication strategies for processing nacre-like composites. We also try to explain why natural materials work so well and see how we can implement these lessons in synthetic composites. Finally, we provide an outlook on the new trends and ongoing challenges in this field. We hope this Account will inspire future developments in the field of ice-templating and bioinspired materials.



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■ INTRODUCTION

Nacre, the biocomposite covering the inside of many species of shellfish, is probably the flagship model of complex composites in materials science. Since scientists first realized how damage-resistant nacre is, hundreds if not thousands of studies have addressed the structure/property relationship of nacre and synthesized damage-resistant materials inspired by the structure of nacre. Nacre, like many natural composite materials, has toughness values that far exceed those of its constituents and their homogeneous mixtures, defeating the rule of mixtures. Nacre's microstructure evolved over 400 million years ago in the world's oceans, suggesting that an optimum was reached through evolution. Nacre is an assembly of aragonite ($CaCO_3$) bricks separated by a protein layer (Figure 1). Nacre can be classified as a brick-and-mortar material. The bricks, made of an assembly of nanoparticles, are fairly complex, with variations of thickness and mineral bridges linking adjacent bricks. Each of nacre's microstructural features induces energy dissipation mechanisms when a crack propagates through the structure.

Inspired by this complex, hierarchical architecture, many processing routes have been proposed to replicate one or several of these structural features: top-down (gluing layers together), or bottom-up (layer-by-layer deposition). No single route can address all the requirements, and each one comes with limitations in terms of complexity, sample size, processing time, scalability, and possible materials combinations. In this context, we introduced freezing techniques as a path

to build such complex composites in 2006. [1] The concept, initially demonstrated with ceramic/polymer or ceramic/metal composites, was later extended to ceramic/ceramic composites. [2] We now focus our research on the fundamental understanding of the physics at play during freezing, [3] laying the foundations for the processing of engineered living materials.

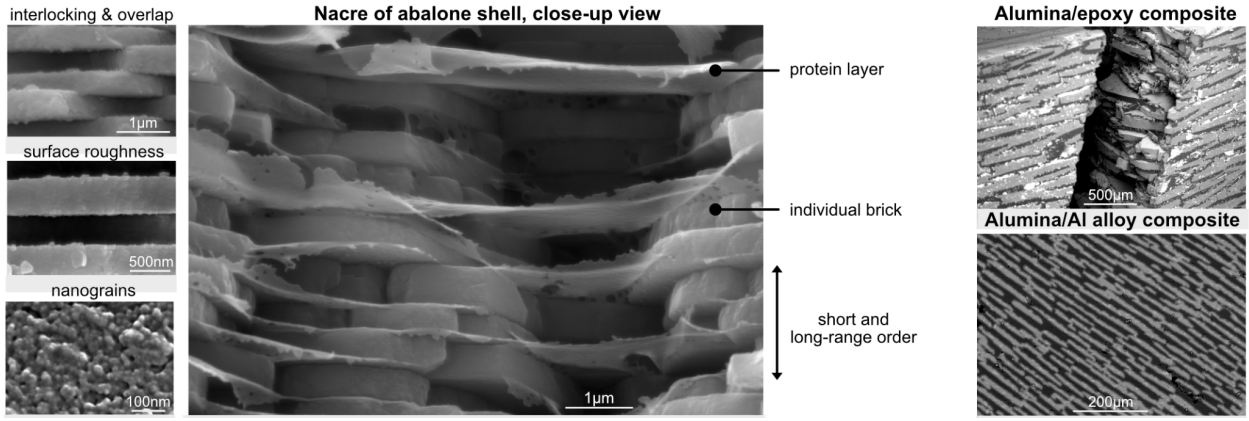


Figure 1. The complex structure of nacre in abalone shell and the first complex composites obtained by freezing. Only a part of the microstructural complexity was initially reproduced. The alumina composites shown here were obtained during the study reported in [1]. Reproduced from 10.6084/m9.figshare.18741092 © (2022) S. Deville, CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

■ FREEZING AS A PATH TO BUILD COMPLEX COMPOSITES

When a suspension of colloidal particles is frozen, particles are rejected by the growing ice crystals and concentrate in the spacing in between. This phenomenon is well-known and documented in very different contexts, ranging from the freezing of soils in cold regions to the preparation techniques of soil samples in geophysics studies, or freezing-based treatments of sludges[4]. In materials science, freezing could be harnessed to prepare porous materials. After the ice is freeze-dried, the resulting scaffold is a porous body, with porosity templated by the ice (the approach that is now referred to as ice-templating[5]).

In 2006, in a proof-of-concept study[1], we took advantage of the ice-templating approach to build complex composites. We infiltrated ice-templated porous ceramics with a second phase (metal or polymer). This approach provided multi-layered, lamellar complex composites with a microstructure reminiscent of nacre (Figure 1). The resulting composites exhibited a marked crack

deflection during crack propagation, enhancing the damage resistance (toughness) of the materials, offering an interesting trade-off of strength and toughness.

Freezing became a new approach for making brick-and-mortar materials, with several advantages. The first is the versatility of the approach: the ice-induced segregation is based on physical interactions and is thus in principle material-agnostic. The second main advantage is the number of levers available to control the morphology and the microstructure of the materials, inheriting features defined by ice physics and the interaction of particles with the ice. Many of these features (surface roughness, mineral bridges) are, to some extent, encountered in nacre, and provided hope that hierarchical synthetic materials could be prepared with this approach.

The technical requirements for the processing are low, and can easily be set up in a new lab. Unidirectional freezing can be easily performed with a source of cold, which can be achieved by a standard cooler, a source of liquid nitrogen, or a Peltier module. Additional control can be gained by controlling the freezing rates or gradients. [6] A standard freeze-dryer is then needed to sublimate the ice before further densification treatments.

The freezing technique filled a gap compared to the other processing routes for brick-and-mortar materials. Because self-organization occurs in the bulk during unidirectional freezing, the processing time (typically minutes) is much shorter than the layer-by-layer deposition approaches, and cm-sized samples can be prepared easily. Finally, the typical layer thickness achieved with this approach (typically 5–100 μm) is neither in the nanoscopic range (nm), nor in the macroscopic range (100 μm-several mm), a thickness range critical to achieving an optimal damage resistance of the materials. This initial proof of concept opened a new line of research for the development of complex composites.

■ UNDERSTANDING AND CONTROLLING FREEZING

Control of the microstructure and process parameters

We initially devoted our research efforts to understanding the freezing process and particle redistribution, which ultimately control the microstructure and thus the properties of the materials. Cracks, sometimes encountered in the final structure, affect mechanical performance. *In situ* investigations by X-ray radiography and computed tomography revealed that these cracks appear during freezing and are the result of particles' accumulation at the freezing front and instabilities

of the front[7,8], which can be controlled by adjusting process parameters such as the front velocity, the particle size, and the added polymer binders.

The control of ice growth to adjust the final microstructure was quickly demonstrated. When water turns into ice, lamellar ice crystals with dendritic surfaces are formed (see Fig. 3c for example), because of the anisotropic growth rate of the ice crystals. A simple approach to modify the growth morphologies of the ice crystals was the addition of solutes (salt, sugar, glycerol)[9]. Although the approach is versatile, it is very hard to use it predictably. A more consistent approach was introduced later, with a specific additive (zirconium acetate) that binds to the ice surface and thus controls its growth morphology in a controllable manner, independently of the nature of the particles used[10].

Freezing is unidirectional. If nucleation is not controlled, a spatially random, heterogeneous nucleation occurs, resulting in domains with locally aligned ice crystals, but no long-range order. If homogeneous anisotropic materials are sought, it is thus essential to control the short and long-range alignment of the ice crystals. We initially tested surface patterning, [9] before developing a freezing under flow approach[2]. More robust reproducible alternatives have since been proposed and in particular, the so-called wedge technique, [11] which has since been reused in several groups. It should also be noted that a fine control of the rheology of the suspensions is not critical. The typical solid loading appropriate for the freezing route are low (10–20 vol%), and thus the suspensions are almost always very fluid.

Improvement of mechanical properties

Building upon this initial proof of concept, in later studies we and other groups focused on exploring the concept and improving the microstructure and mechanical properties of such composites (Figure 2). Several compositions and approaches were explored to produce metal/polymer and metal/ceramic composites exhibiting the highest toughness to date, including for example alumina/PMMA and alumina/aluminum.

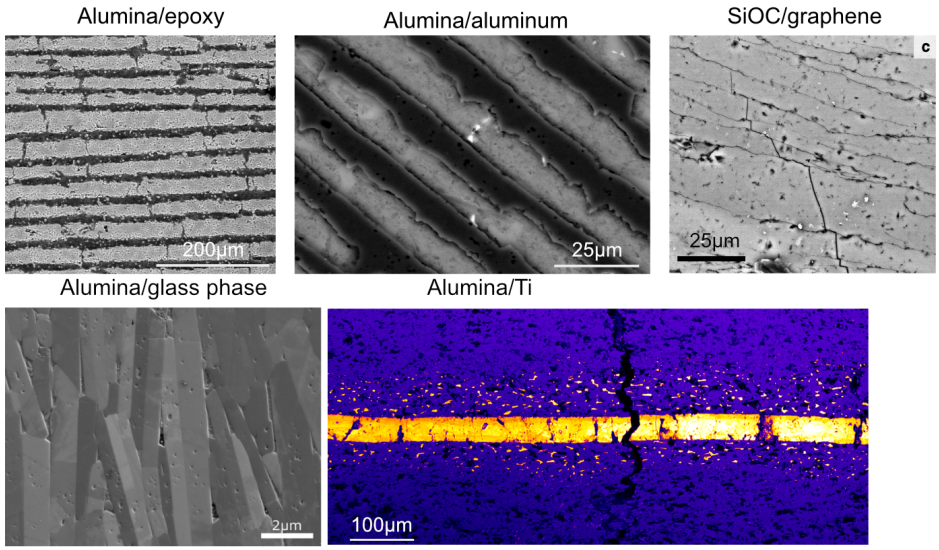


Figure 2: Microstructures of different types of composites built through freezing. Alumina-epoxy [1], alumina-aluminum [1], SiOC/graphene (Reproduced with permission from [12] © 2017, The Authors), alumina/glass (same material than in [2], Reproduced from 10.6084/m9.figshare.11907276 © 2020 S Deville et al.), alumina/Ti[13] (Reproduced with permission © 2016 S Deville)

At the same time, the control of several microstructural features and their impact on the properties were investigated, including the role of platelets surface roughness[14] and the addition of bridges. [15] Model materials were developed to investigate each feature separately, providing guidelines for the design of complex composites. The mechanical properties were dramatically improved with a simple trick: pressing the porous body unidirectionally before infiltrating it with a second phase[16]. This pressing step reduces the amount of porosity before infiltration, and thus shifts the ceramic/polymer ratio to higher ceramic content (60–80 vol%). Both the damage resistance of the composite and its strength were improved, with an R-curve toughness of to 30 $MPa.m^{1/2}$ and a yield strength up to 200 MPa. However, due to the difficulty of infiltrating liquid metals into small pores, this approach is limited to ceramic/polymer composites.

Exploration and control of the underlying physics

The sequence of solidification events translates directly into the microstructure and must be understood and controlled. Several studies, based on *in situ* observations techniques, investigated how the physics of freezing takes place in these particular systems (Figure 3). The initial events, nucleation and growth, lead to a steady-state growth of the ice crystals, and result,

for example, in a gradient of the sample[17], which can be either removed to maintain a constant open porosity or used, for example in membrane filtration applications.

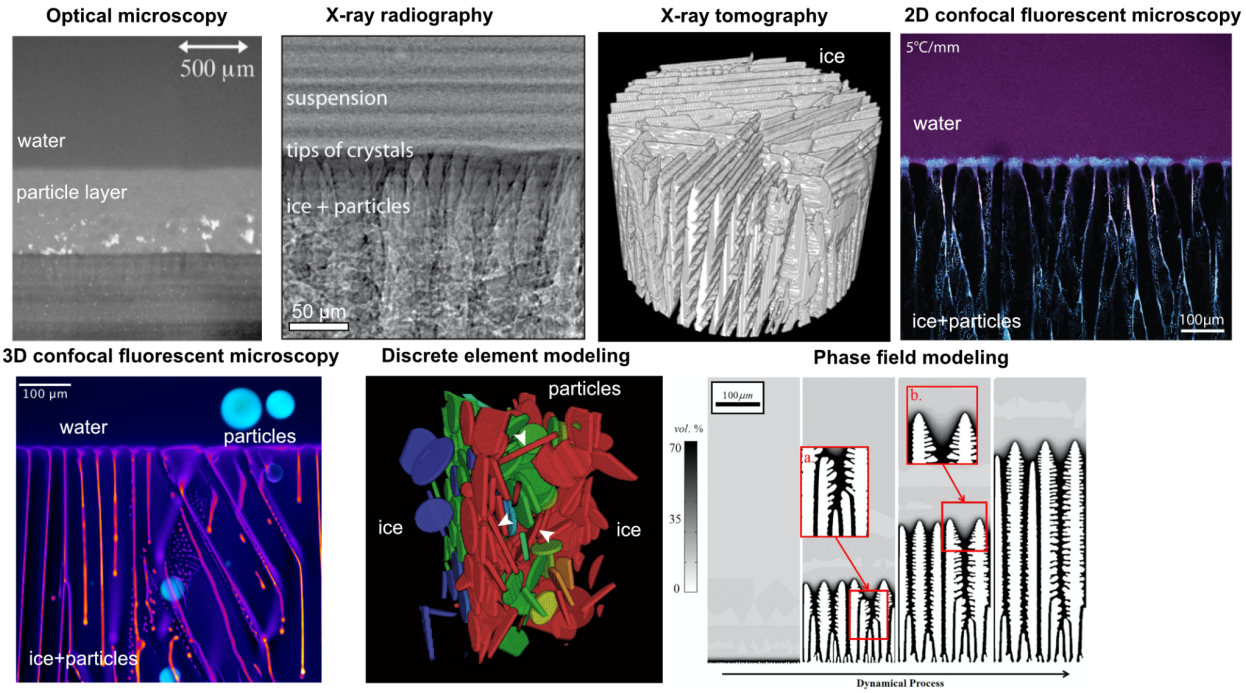


Figure 3: Observation techniques and modeling approaches. The phenomena must be addressed at different scales to fully comprehend the underlying physics. Optical microscopy (reproduced with permission from [18] © 2017 American Chemical Society), X-ray radiography and tomography (reproduced with permission from [19] © 2020 Elsevier), 2D and 3D confocal microscopy [20] (reproduced from 10.6084/m9.figshare.5722675 © 2020 S Deville et al,), discrete elements modeling (reproduced with permission from [21], © 2014 American Chemical Society), and phase field modeling (reproduced with permission from [22] © 2017 WILEY-VCH).

One of the keys to understanding the phenomena (crystal growth, particle redistribution) taking place during freezing is the ability to image them *in situ*, during solidification. This requires ideally 3D imaging at submicronic resolutions of ice crystals growing relatively fast (5-20 µm/s). We initially used X-ray radiography[23,24], followed by complete 3D imaging of the frozen sample. Further developments provided *in situ* 3D imaging of the growing ice in a colloidal suspension[19], although the spatial resolution was insufficient to image the colloidal particles. At this point, the interaction of the X-ray beam with the ice, very sensitive to small changes of temperature, also became an issue that prevented its further use up until this point in our research.

Physics provided the path to understanding the freezing of suspensions, and the fundamentals of particle interactions with the freezing front were investigated under carefully controlled conditions. We demonstrated, in particular, why a layer of concentrated particles accumulated at the tip of the ice crystals that appear in the steady-state of solidification[18], and the role of the boundary conditions (e.g., the mold and its characteristics) on the development of this layer[25]. This layer is one of the keys to understanding how microstructural defects develop in the final materials. More recently, phase field modeling has been used to predict the microstructural morphology maps[22].

Limits of the initial approach

These initial developments faced several limits. First, the ceramic layers in these complex composites are polycrystalline. The strength of a polycrystalline brick is much lower than that of a single crystal. The second limit is the typical thickness of layers that can be achieved with this approach, slightly smaller than 10 μm. The brick thickness in natural nacre, considered an ideal target, is twenty times smaller. Bricks (or layers) too thick or too thin will only provide a limited crack deflection, although this depends on the composition and individual properties of the bricks and of the mortar[26]. Because nature had millions of years to optimize the thickness of platelets, there is a consensus that the nacre platelets' size is an optimum with respect to the constituent properties. Strangely, this has not been demonstrated (e.g by the fracture mechanics community). Another issue is the (still) relatively high fraction of ductile phase (20–60 vol%, depending on the processing route), which limits the maximum strength of the composites. The best approaches rely on pressing the ice-templated structures. Reaching higher densities before the infiltration of a second phase requires a smooth wall's surface and long-range order of the lamellar walls (and thus crystals). Finally, the development of brick-and-mortar composites relies on an optimal adjustment of the interfacial strength between the bricks and the mortar. If the mortar strength exceeds the strength of the ceramic bricks, the bricks will fracture; this will eliminate the extrinsic toughening generated by crack bridging and brick pull-out, resulting in a catastrophic fracture. However, it remains extremely difficult to engineer precisely the interfacial strength and the mortar strength in these complex composites, the optimization of the properties still relies on trial and error approaches, as there are no simple guidelines to follow.

■ FROM ICE-INDUCED SEGREGATION TO SELF-ORGANIZATION AND SELF-ASSEMBLY

The growth of ice crystals and corresponding segregation of particles was initially performed with particles with uncontrolled and approximately isotropic morphologies. When such particles are segregated, concentrated, and packed between the crystals, no particular organization is observed.

Alignment of anisotropic particles

A step forward in the complexity was achieved with the use of anisotropic particles. They can be used to further control the microstructure of the materials. The platelets in nacre are typically 10–20 μm long (diameter) and 0.5 μm thick, although these values depends on the nacre type[27]. We tested two anisotropic systems in this size range: alumina and boron nitride. The platelets suspensions can be frozen under conditions where the platelets align with short-range order. The alignment also depends on the local spacing between the crystals[21], and either compact (with all particles aligned through the thickness) or sandwich structures (with dense outer layers and less dense cores) can be achieved. Discrete elements modeling was used to understand these behaviors and successfully guide the choice of the ideal processing conditions. Two types of porous materials were obtained with walls made of aligned platelets: alumina[28] and boron nitride[21], with anisotropic thermal conductivity resulting from the texture of the aligned platelets. The ultimate objective was nevertheless the use of this phenomenon to align platelets and obtain dense, textured composites, discussed later in this paper.

This approach was extended afterward to other types of anisotropic objects and in particular fibers[29]. Because of their aspect ratios, fibers percolate into a 3D structure at a low concentration. Ice-templated porous materials made of fibers present an interesting combination of rigidity, high porosity, and low pressure drop, which could be useful in, for example, filtration applications.

Self-assembly

The alignment of platelets or fibers is not a self-assembly phenomenon. Proper ice-induced self-assembly was demonstrated later, by freezing block copolymers aqueous systems (Figure 4). The segregation of monomers by the growing crystals increases their local concentration progressively, eventually triggering their self-organization into micelles, which themselves

organize into crystalline phase upon further increase of the concentration[30,31]. Although the process was not used to create complex composites as discussed in this paper, it nevertheless added self-assembly to the microstructure control toolbox. Harnessing such self-assembly could be used to further increase the complexity of the composites obtained by freezing, which is unexploited to date.

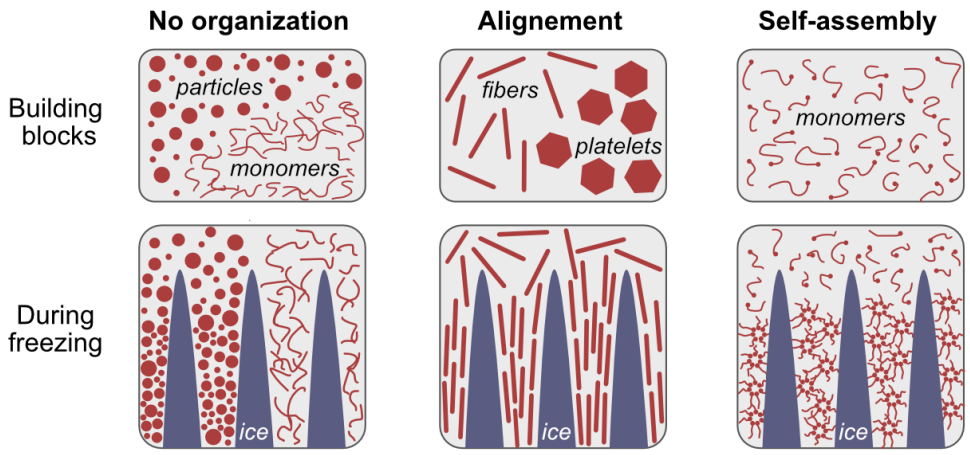


Figure 4. From ice-induced segregation to ice-induced alignment and self-assembly. Objects such as ceramic particles or monomers are segregated and concentrated between the ice crystals (left). Anisotropic objects, such as fibers or platelets, can get aligned during ice growth (center). Monomers of block copolymers can be concentrated between the ice crystals, leading to their self-assembly into micelles and more complex architectures. (Reproduced from 10.6084/m9.figshare.18741092, © 2022 S. Deville).

Concluding remarks on this section

All these results demonstrated the interest in and the versatility of freezing to obtain complex composites. From a physical point of view, the approach could be described as just another way to concentrate building blocks, but with more possible refinements (e.g. phase separation patterns). Another specificity of these approaches is the low temperature of the process (below 0°C). If there are no obvious specific advantages when working with ceramic particles, this temperature range could be a strong asset when engineering complex composites for biomedical applications, where drugs, cells, or other living elements are incorporated. These aspects are discussed in the final section of this paper.

■ NACRE-LIKE ALUMINA

The commercial availability of alumina platelets was a game-changer in the development of complex composites by freezing.

A new class of bioinspired brick-and-mortar materials

We took advantage of the ice-induced segregation and alignment of platelets to obtain dense, inorganic composites with a complex architecture and microstructure, replicating several of the morphological features of nacre[2]. These materials were thus naturally named nacre-like alumina. Using these alumina platelets permitted us to simultaneously solve three problems:

- Because each brick is made of a single crystal, the strength of the brick, and thus of the final composites (470 MPa), is much higher.

- The bricks' thickness (around half a micrometer) is an order of magnitude smaller than with the previous approaches. This lengthens the crack path upon crack propagation and is believed to further improve the damage resistance of the material.

- Because it is easier to pack platelets with a smooth surface, materials with a higher fraction of platelets are obtained after pressing and sintering. The final brick-and-mortar composites have a final phase repartition closer to that of nacre, with 95–98% ceramic platelets, and 2–5% of mortar (here a glass phase). This is another major source of strength increase in the final composite.

- The surface roughness of platelets and the presence of mineral bridges between adjacent platelets are essential toughening features of nacre. Small amount of nanoparticles can be added to the platelets suspension. The heteroaggregation of the platelets and nanoparticles can in principle provide both the desired surface roughness and the formation of bridges. The beneficial role of these nanoparticles was confirmed later in separate experimental[15] or modeling studies[32].

However, this initial development came with limitations, including a complex processing route (freezing-under-flow, not easily transferable to another lab or scaled up) and small sample thickness (mm). This forced the development of alternative processing routes to achieve the same microstructure. If the ice crystals can induce a local alignment of the platelets, a long-range order is required to enhance the packing and densification of the microstructures. Several solutions (surface patterning, freezing under flow, wedge technique) have been proposed to control the ice

nucleation and thus create long-range order. The wedge technique[11] seems to be the most appropriate for scale-up. It was also difficult to precisely control the homogeneity of the microstructure (unlike processes where layers are deposited one by one, for example), leading to spatially varying mechanical properties. The role of such heterogeneities may not be critical for all applications but needs to be carefully assessed.

Mechanical properties of nacre-like alumina

These composites exhibit interesting toughness values, better than that of alumina. The damage resistance of these composites can be defined by several parameters. The first (and easier to measure) is the fracture toughness (K_{Ic}), which is approximately 6 MPa.m^{½}, and thus higher than that of a standard alumina (4 MPa.m^{½}). The main feature of interest, however, is their R-curve (increase of toughness) upon crack propagation. Nacre-like alumina reveals a constantly increasing R-curve, meaning that propagating a crack becomes more and more difficult. The measure is in principle valid up to a given crack length, and the maximum toughness measured at this point has been often used as a toughness measurement.

The trade-off between strength and toughness in nacre-like alumina fits a fairly unique spot in ceramic composites: because these complex composites are made of mineral only (typically 95% alumina platelets, with the remaining 5% alumina nanoparticles and a glass phase), the strength (470 MPa) is typical of a standard ceramic (but much higher than that of metal/ceramic or polymer/ceramic brick-and-mortar composites), but its toughness is much higher. Combined with their hardness, corrosion resistance, and preservation of properties up to several hundred degrees, these complex composites could thus make their way to structural applications in demanding environments.

These characteristics raise many questions, both fundamental and practical. Which toughening mechanisms contribute to the damage resistance observed? What is their relative contribution? How critical is it to achieve a homogeneous microstructure? Does the toughness of these composites depend on more than simple crack deflection at the brick/mortar interface?

We evaluated the properties of these composites at different length scales (Figure 5). Macroscopic tests (single-edge notched beam and R-curve) on large (cm-sized) samples[33] validated the properties at a larger scale while revealing the limitations of measurements performed

previously on small (mm-sized) samples. Microscopic bending tests, performed on focussed ion beam-machined cantilevers, were used to evaluate the properties depending on the relative orientation of the cracks and the platelets[34]. Nanoindentation, performed at the surface of the samples[35], was used to evaluate the influence of the orientation of the platelets on the micro-mechanical properties.

Discrete elements modeling (DEM) was implemented to model crack propagation in these complex composites[36]. Although many micro-mechanical models had been proposed previously to understand the properties of brick-and-mortar materials[37], DEM can naturally implement topological modifications such as crack propagation, crack branching, or multiple cracking, and is thus useful to understand the extrinsic toughening mechanisms acting during crack propagation. DEM can guide the microstructural design such as the relative mechanical properties of the brick and the mortar, the role of adhesion between them, or the density of inorganic bridges between the platelets[32]. These studies revealed that the mechanical properties of these materials were probably not at their optimum yet. The interface strength between the platelet and the mortar, for example, is currently too low[36]. The models have since been made more realistic by generating real microstructures, using actual micrographs of nacre-like alumina[38]. It should also be noted that this is a complex, multi-parameters optimization problem. Because several parameters and features can be adjusted, only local optimum can be achieved[32]. The biggest challenge now is to implement such fine adjustments of the microstructure and composites properties in the actual processing routes of these composites.

Fracture mechanics have also been helpful to understand the mechanical properties of these composites and measure properties difficult to access otherwise. The combination of large-scale and small-scale experiments, for example, can provide a measure of the interface tensile and shear strength (between the bricks and the mortar), extremely difficult to access otherwise[39], as well as a more reliable fracture toughness measurement taking into account the anisotropy in the properties of these materials. This fracture mechanics analysis relies on the application of the so-called coupled criterion: both stress and energy conditions must be fulfilled for a crack to nucleate and propagate in the material.

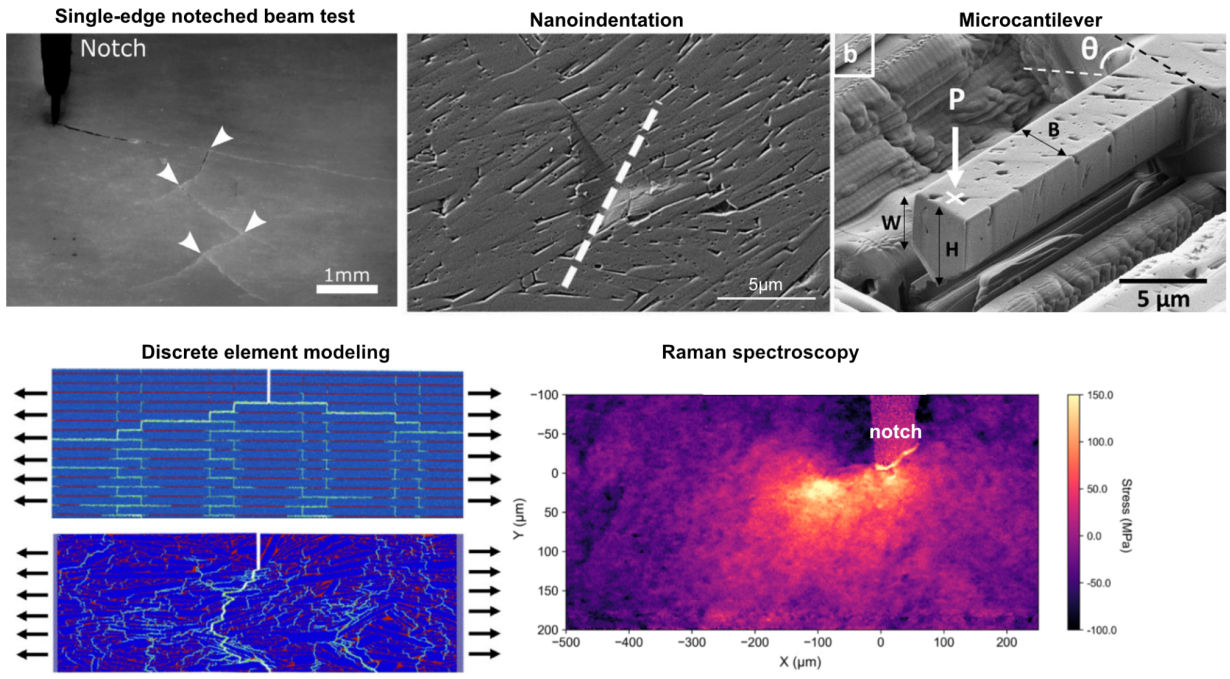


Figure 5: Understanding the mechanical properties of these complex composites. Complementary analysis at different scales is required, from macroscopic tests (SENB[33] and R-curves measurements) to smaller scale (nanoindentation[35] and microcantilever[34]), modeling (discrete element modeling[38]) and Raman spectroscopy[40].

SENB, microcantilever: Reproduced from 10.6084/m9.figshare.11907276, 10.6084/m9.figshare.11999985.v1 © (2020) S. Deville. Nanoindentation: Reproduced with permission from [35] © 2020 Elsevier. Discrete element modeling: Reproduced with permission from [38] © 2020 Acta Materialia Inc. Published by Elsevier Ltd. Raman spectroscopy: reproduced with permission from [40] © copyright The Authors.

Improving the microstructure and properties

Several strategies have been demonstrated to improve the microstructure and/or the mechanical properties, taking advantage of ceramic processing and control of the microstructure. Zirconia, for example, can be added as secondary particles to increase both the strength and the toughness[41]. The improvements are due to both residual stresses (due to the mismatch of thermal expansion coefficients) and transformation toughening. A better control of the spatial repartition of the building blocks (alumina nanoparticles and platelets) can be achieved by hetero-aggregation[42]. Finally, a key feature of these composites is the interface between the platelets and

the mortar. Adjusting its composition[43] can bring noticeable improvements to the mechanical properties.

Nacre-like alumina without freezing

Alternatives to freezing have thus been reported, including pressing (platelets align under the uniaxial pressure[44]), sedimentation (platelets align at the top of the sediment[45]), or magnetic field-assisted slip casting (platelets are functionalized with magnetic nanoparticles and the application of a magnetic field forces the alignment of the platelets[46]). These routes are much simpler and scalable and enable in particular the processing of samples of several centimeters in diameter and thickness. If freezing was initially used as a mean (align platelets locally) to an end (nacre-like microstructure), it is clear today that some of these alternative processing routes, and in particular uniaxial pressing, are easier to implement than freezing techniques at both lab and industrial scales. The quality of the texture (grain orientation, quantified by EBSD) is sufficiently close to yield similar mechanical properties[47].

Concluding remarks on nacre-like alumina

The state of the art of these materials was recently reviewed by F. Bouville[47]. Among the many questions raised in this review and our paper, two are particularly intriguing and critical. First: have we reached the optimum of these materials? The toughening mechanisms result from the interplay of several mechanisms and properties of the microstructure (adhesion strength between the platelets and the glassy phase, relative Young's modulus, dimensions of the glass phase, presence and characteristics of the mineral bridges, etc). Although some of these parameters have been explored separately, it is unlikely that we have reached the optimum yet. Since we try to optimize several mechanical properties at once, it is likely that only local optimums exist, with trade-offs to be made. This is in particular supported by discrete elements modelling[32]. The second intriguing question is the optimal dimension of the platelets. All the developments of nacre-like alumina were enabled by the availability of alumina platelets of the same dimensions as that of the aragonite bricks in nacre. We can thus wonder whether this should be the optimal size. Micromechanical models[26] have shown that the optimal size and aspect ratio of platelets may depend not only of the nature of the materials used, but also on the mortar strength. Testing the validity of such models would require access to platelets of the same material but of different dimensions.

■ CURRENT TRENDS AND POSSIBLE FUTURES

Nacre-like alumina

Questions of interest can be classified into four categories:

- Morphology of the platelets: all experimental studies rely on the availability of platelets. Although several dimensions and aspect ratios are available and have been tested, all platelets share a common characteristic: their thickness is constant. In nacre, the platelets exhibit a certain waviness, which enhances the mechanical properties when the structure is loaded[48,49]. Engineering such morphologies into monocrystalline platelets may nevertheless be extremely challenging.

- Composition: previous studies, in particular on brick-and-mortar materials, revealed the excellent properties of metal/ceramic composites. Nacre-like alumina with a metal interphase would certainly be interesting to test. We performed preliminary testing of nacre-like alumina with Ti interlayers[13], although it turned out to be a poor choice and the mechanical properties were disappointing. Ni seems to be a better choice[50]. Although several types of platelets have been used (alumina, BN, glass), most of the work has been done on alumina platelets, because of their appealing morphologies and interesting mechanical properties. Having also platelets stronger than alumina, such as silicon carbide or zirconia, would most likely improve the strength and toughness of these composites.

- Process: several processes have been reported to align the platelets. There is a strong interest in processing routes that would be able to control the local alignment of the platelets (critical for densification and local crack deflection) while also enabling other microstructural features (variations of long-range alignment, complex shapes of pieces). Additive manufacturing routes are of course of interest here, with shear-induced alignment of platelets upon deposition through a nozzle[51].

- Characterization: both the microstructure (defined at several levels) and the properties need to be thoroughly characterized. This characterization includes small-scale analysis[41] and fracture mechanics analysis adapted to materials showing extensive crack deviation. We also recently applied Raman imaging to image *in situ* the stress fields during crack propagation[40], which is helpful to understand the relative contributions of the various toughening mechanisms.

Beyond nacre-like materials: other freezing-based processes

Freezing is not used in the latest nacre-like alumina developments. The main steps of the freezing-based processing routes available are shown in Figure 6. Several freezing-based ideas nevertheless await further developments. Two main ideas could, in particular, be fruitful:

- Taking advantage of freezing-induced self-assembly[30] to achieve more complex microstructures. Self-assembly has been limited so far to block copolymers systems (to template mesoporosity), but any type of self-assembly could in principle be triggered by freezing.

- One of the strengths of freezing is the possibility to combine it with other processes. A few recent examples include additive manufacturing[51], salting out[52], or biomineralization[53]. Such combinations are useful to achieve complex compositions and microstructures.

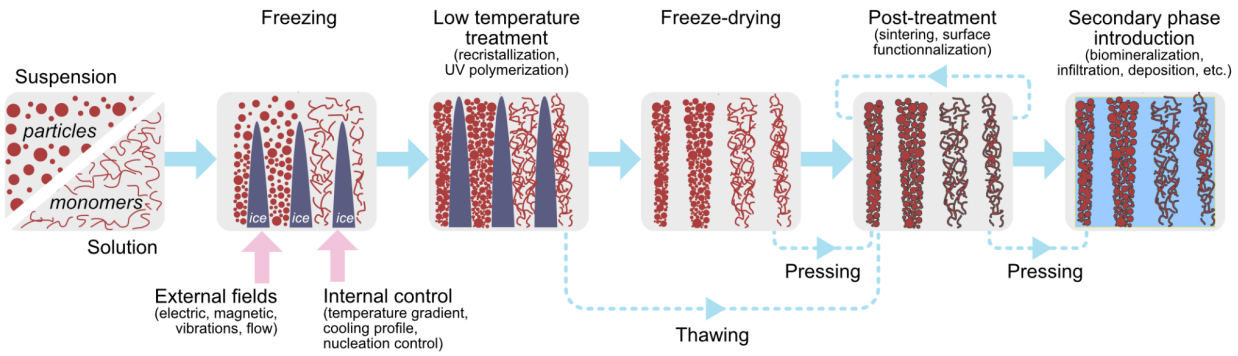


Figure 6: Schematic of the main steps of the freezing-based processing routes available. Reproduced from 10.6084/m9.figshare.18741092, © 2022 S. Deville.

Laying the foundations for soft matter complex composites

The developments discussed so far in this review were strongly anchored in the engineering materials communities, and in particular ceramic and metals processing. A different class of complex composites is quickly gaining interest: engineered living materials[54], developed in the soft matter and biology communities. The material-agnostic nature of the freezing routes, combined with the use of an aqueous system, the absence of solvents, and the low temperatures being used, are all strong assets for the development of such complex composites. More complex building blocks, such as cells or bacteria, can be frozen[55]. Understanding the fundamental mechanisms controlling the interactions between the crystals and the objects, as well as the fate of

soft objects is essential in this context. . We recently focused on two related aspects of these problems:

- Understanding the physics of ice interacting with soft objects and the various components added to the initial mix (solutes, surfactants, cryoprotectants, etc.). Cryoconfocal microscopy[3] is particularly appropriate for such studies, revealing self-assembled objects in a temperature gradient[56], the key role of solute[57], or the importance of the relative thermal conductivity of the particles and the melt[58]. These studies contribute to a better understanding of the formation of the microstructure and the parameters that control it.

- The behavior of soft objects at the freezing front. Soft objects can deform (and heal or not), coalesce, grow, shrink, or lose their integrity (cells) upon interacting with the front. Their survival and functionality in the final complex composites are directly related to their physicochemical environment during freezing, as we recently reported with yeast cells[59] frozen in the presence of alginate. The list of questions that must be addressed expands rapidly.

Applications

Despite hundreds (or thousands) of papers and many claims of possible applications, no applications of these materials exist so far. Bringing a lab innovation to the market is a much more complex endeavor than most people realize. Reproducibility, for example, is often paramount and yet rarely reported (probably because it involves tedious work). Intellectual protection through patents is also one of the early keys. The number of patents related to freezing-based approaches for such materials has steadily increased over the years. To succeed, novel composites must present either an enormous gap in terms of properties (to justify their adoption), or be able to match the properties of existing solutions at a much lower cost. Either way, having scalable, cost-effective routes is often a key to success. Novel materials are generally more likely to succeed if they are obtained using already industrialized tools and processes.

After 20 years of research on the topic, we now have a much clearer view of what can be achieved with these approaches, in terms of materials, microstructure, properties, and processes. Most likely, applications may appear first where an important value is added, or where the cost is less critical. A first application analysis was recently reported[60], evaluating the potential of nacre-like alumina as a replacement for Ni superalloys in aircraft's engine. The authors concluded that although similar properties, engine performance, and life cycle sustainability could be achieved,

the reliability, shaping, repair, and governance of the production process remain limiting and require further progress and improvements. There are usually and unfortunately little incentives for academics to investigate such aspects. Alternatively, lessons can certainly be learned from a domain where freezing-based routes are routinely used at very large scales to process relatively cheap materials: food engineering and the frozen food industry.

■ CONCLUSIONS

Freezing as a path to build complex composites turned out to be a rich line of research and developments and is now a formidable toolbox with many advantages, both in terms of process (low temperature, relative material independence) and microstructures. As with any tool, future progress will likely emerge from the combination with other tools, such as additive manufacturing. Understanding and controlling the freezing routes and associated phenomena is a multidisciplinary endeavor. Knowledge and techniques from materials science, physics, chemistry, physical chemistry, and biology are required, making it an appealing (albeit complex) topic for many groups worldwide, with both great science and potential applications in the future.

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