ESRF	**Experiment title:** Study of the freeze casting process by 3D imaging during freezing and sintering	**Experiment number:** MA506
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Report:

[1] Deville S, Maire E, Lasalle A, Bogner A, Gauthier C, Leloup J, Guizard C. In situ x-ray radiography and tomography observations of the solidification of aqueous alumina particle suspensions-part i: initial instants. Journal Of the American Ceramic Society 2009;92:2489-2496. This paper investigates by in situ high-resolution X-ray radiography and tomography the behavior of colloidal suspensions of alumina partic les during directional solidification by freezing. The combination of these techniques provided both qualitative and quantitative information about the propagation kinetic of the solid/liquid interface, the particle redistribution between the crystals and a particle-enriched phase, and the three-dimensional organization of the ice crystals. In this first part of two companion papers, the precursor phenomena leading to directional crystallization during the first instants of solidification are studied. MullinsSekerka instabilities are not necessary to explain the dynamic evolution of the interface pattern. Particle redistribution during these first instants is dependent on the type of crystals growing into the suspension. The insights gained into the mechanisms of solidification of colloidal suspensions may be valuable for the materials processing routes derived for this type of directional solidification (freeze-casting), and of general interest for those interested in the interactions between solidification fronts and inert particles.

[2] Deville S, Maire E et al., In situ x-ray radiography and tomography observations of the solidification of aqueous alumina particles suspensions. part ii: steady state. J Am Ceram Soc 2009;92:2497-2503. This paper investigates the behavior of colloidal suspensions of alumina particles during directional solidification, by in situ high-resolution observations using X-ray radiography and tomography. This second part is focussed on the evolution of ice crystals during steady-state growth (in terms of interface velocity) and on the particle redistribution taking place in this regime. In particular, it is shown that particle diffusion cannot determine the particle concentration profile in this regime of interface velocities (20-40 $\mu m/s$). Particles are redistributed by a direct interaction with the moving solidification interface. Several parameters controlling the particle redistribution were identified, namely the interface velocity, the particle size, the shape of the ice crystals, and the orientation relationships between the crystals and the temperature gradient.

[3] Deville S, Maire E et al., Metastable and unstable cellular solidification of colloidal suspensions. Nature Materials 2009;8:966-72.
Colloidal particles are often seen as big atoms that can be directly observed in real space. They are therefore becoming increasingly important as model systems to study processes of interest in condensed-matter physics such as melting, freezing and glass transitions. The solidification of colloidal suspensions has long been a puzzling phenomenon with many unexplained features. Here, we demonstrate and rationalize the existence of instability and metastability domains in cellular solidification of colloidal suspensions, by direct in situ high-resolution X-ray radiography and tomography observations. We explain such interface instabilities by a partial Brownian diffusion of the particles leading to constitutional supercooling situations. Processing under unstable conditions leads to localized and global kinetic instabilities of the solid/liquid interface, affecting the crystal morphology and particle redistribution behaviour.

[4] Deville S, Maire E et al., Influence of particle size on ice nucleation and growth during the ice-templating process. J Am Ceram Soc 2010;93:2507-2510. The solidification behavior of suspensions of alumina particles during directional solidification is investigated here by in situ observations using X-ray radiography and tomography. The objective of this study was to assess the influence of particle size on the solidification behavior of the suspensions during the early stages of solidification. Four powders with particle size in the range of 0.2-3.4 μm (median size) were investigated. Solidification is obtained by cooling at a constant rate, starting from room temperature. Attention is specifically paid to the nucleation and growth behavior of the ice crystals in these suspensions. We propose that the nucleation of ice crystals is controlled by the particle size, the surface of the particles acting as nucleation sites. Smaller particle size leads to a lower degree of supercooling because nucleation and growth can proceed at a higher temperature than with larger particles. The initial interface velocity is dependent on the degree of supercooling, and controls the extent of the initial structural gradient in the resulting porous materials.