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Original Article

Multiphase imaging of freezing particle suspensions by confocal microscopy

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ABSTRACT

Ice-templating is a well-established processing route for porous ceramics. Because of the structure/properties relationships, it is essential to better understand and control the solidification microstructures. Ice-templating is based on the segregation and concentration of particles by growing ice crystals. What we understand so far of the process is based on either observations by optical or X-ray imaging techniques, or on the characterization of ice-templated materials. However, in situ observations at particle-scale are still missing. Here we show that confocal microscopy can provide multiphase imaging of ice growth and the segregation and organization of particles. We illustrate the benefits of our approach with the observation of particles and pore ice in the frozen structure, the dynamic evolution of the freeze front morphology, and the impact of PVA addition on the solidification microstructures. These results prove in particular the importance of controlling both the temperature gradient and the growth rate during ice-templating.

1. Introduction

Ice-templating is a well-established processing route for porous materials in materials science in general [1–6] and in ceramics in particular [7–9]. Hundreds of papers are now published every year on the topic, and the structural or functional properties of ice-templated materials are systematically explored [10]. Although a considerable number of applications have been proposed, moving ice-templating from the lab towards industrial applications will depend, to a large extent, of our ability to finely understand and control the process to ensure reproducible, reliable architectures.

Ice-templating is based on the segregation of matter by growing crystals, which can then be concentrated between the later. Removal of the ice–whereby “ice” is a generic term for crystals grown from the solvent–provides a macroporous scaffold where the pores are a replica of the ice crystals, and the organization of particles in the scaffold is obtained during freezing. The structure of ice-templated materials, and thus their properties, are therefore largely controlled by the phenomena that takes place during freezing.

A lot of attention has thus been paid to in situ observations of the freezing of particle suspensions. Several techniques have been proposed, each having its advantages and limitations [11]. Most of what we understand from the interactions of particles with growing crystals have been obtained by optical microscopy [12,13]. However, it only provides 2D observations, and the spatial resolution is not sufficient when small particles are used. X-ray imaging can provide 3D reconstruction of the grown [14,15] or growing [16] crystals. However, its spatial resolution is not sufficient either to image particles. Artifacts induced by the beam are also still problematic [16]. Transmission electron microscopy has also been used [17] but does not provide 3D observations, and is not appropriate for systematic experiments. As the sample is fixed and of small dimensions, only a few interactions events can be imaged.

In absence of appropriate experimental observations, efforts have been put in modelling the redistribution of particles by growing crystals. Discrete elements modelling, in particular, provided numerous insights into the physics of ice-templating. The role of the growth rate of the crystals on the ordering of monodispersed spherical particles [18] or the alignment of anisotropic (platelets) particles [19], was assessed. These results can be used experimentally to produce a variety of materials with controlled microstructures and functional or structural properties [20]. Further progress in our understanding now depends on in situ observations of these phenomena.

Ideally, we need thus a technique able to image in situ and without artifacts the growth of ice crystals and the redistribution of particles, as well as the later stages of freezing when ice invades the pores between concentrated particles. We recently demonstrated how confocal microscopy could be used to image in situ in 3D the growth of ice crystals [21]. Here we built on this preliminary work and show that particles can also be imaged during freezing. We developed a cooling stage that provides an independent control of the temperature gradient and the growth rate of the ice crystals, making systematic investigations possible. In this paper, we demonstrate the benefits of this approach to investigate the physics of ice-templating.

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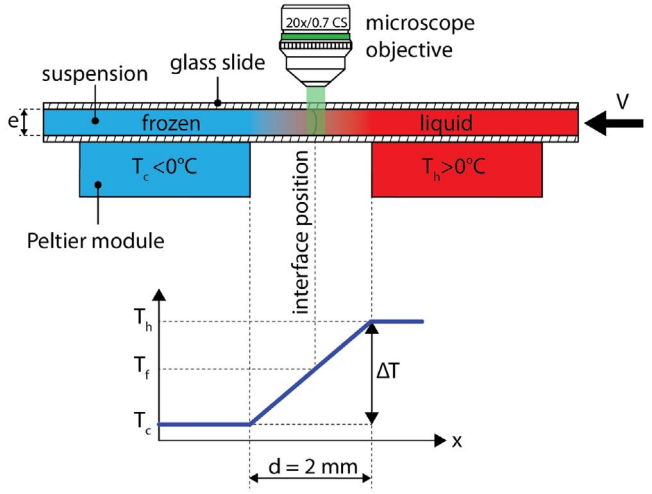

Fig. 1. Experimental setup to perform in situ freezing experiments in the confocal microscope. A constant temperature gradient $\Delta T = T_h - T_c$ is established in the gap d between the Peltier modules. The sample is translated through the temperature gradient at a constant velocity V, which induces a growth of the ice crystals at a velocity V. The interface is thus kept at a constant position in the observation frame. Samples are 100 µm thick. T_f is the freezing point of the suspension.

2. Methods

We used 2 µm diameter PMMA/TEFMA particles, marked in fluorescence with Pyrromethene 546 (emission wavelength: 519 nm). The fluorescent dye (Sulforhodamine B) is dissolved in water at 10^{-4} M. The suspensions were then prepared by incorporating 1 vol.% of particles in this aqueous solution. The particle concentration is lower than that typically used in ice-templating (5–40 vol.%) because we cannot properly image a volume if the particle concentration is too high, because of light scattering. Using index-matched particles would be more ideal for imaging, but this means not using pure water as index matching is usually obtained in water/DMSO systems. We prefer to use suspensions which formulation (aqueous) is close to that of ice-templating. The suspensions were sonicated in an ultrasound bath for a few minutes to ensure a good dispersion of the particles. A few suspensions were prepared by dissolving 1 wt.% of PVA (POLYVIOL SOLUTION LL 2830, 25%) in the suspension.

We developed a cooling stage to perform in situ freezing experiments under the confocal microscope. The setup (Fig. 1) is composed of two Peltier modules that provide a constant temperature gradient in the gap d between them. The particle suspension is introduced in a Hele-Shaw cell made of two glass slides, separated by two stripes of double side adhesive tape which act as spacers to ensure a constant sample thickness of 100 µm. The sample is sealed on both sides. This assembly is translated along the x-axis through the temperature gradient at a constant velocity V by a stepper motor (Micos Pollux Drive stepper motor with VT-80 translation stage (PI, USA)). Because the sample is thin (100 µm), thermal equilibrium is achieved in the range of growth rate investigated here (1–50 µm/s); the solidification front is thus at a constant position in the observation frame. We can therefore vary independently the solidification front velocity (adjusted by the stepper motor) and the temperature gradient (established by the Peltier modules).

Confocal imaging is achieved by two different fluorophores: the dye incorporated in the particles, and a second dye (Sulforhodamine B) dissolved in water, which fluoresces at 586 nm. Experiments performed with and without Sulforhodamine B revealed that it has no noticeable impact on the freezing behavior of the system [22]. Images are acquired through two photodetectors, operating at the respective emission wavelengths of the dyes. For image acquisition, we used long working distance non-immersive objectives (Leica HC PL APO 20x/0.70 CS and 10x/0.40 CS2) to minimize the effect of the microscope thermal mass on the freezing process. These objectives have free working distances of 0.59 mm and 2.2 mm respectively.

In a typical experiment, the sample is put in place on top of the Peltier elements, thermal insulation is achieved by covering the sample with a piece of polyurethane foam. A hole in the foam let the objective come in close contact to the sample. The desired temperature gradient ΔT is established by setting the temperatures of Peltier elements and the sample is then put in motion by the stepper motor. The interface velocity stabilizes within a minute after the beginning of the sample translation. The temperature gradient was varied from 5 °C/mm to 15 °C/mm in the experiments. The solidification front velocities were varied from 1 µm/s to 40 µm/s.

Depending on the experiments and features investigated, 2D or 3D images were acquired. Image reconstruction was done with Fiji (ImageJ 1.51h) [23].

3. Results and discussion

The benefits of confocal microscopy to investigate the ice growth and the segregation of particles in a suspension are four-fold:

- we can image individual particles. It is thus possible track the dynamics and organization of particles during and after freezing.
- because the dye is expelled from the growing ice, we can easily discriminate between the water and the ice phases on the images. We can thus image simultaneously the particles, the water, and the ice.
- because of the rapid imaging mode of the microscope, we can image the process in 2D at a rapid time resolution: up to 40 Hz at 512 × 512 pixels. We can thus take snapshots of the solidification microstructures even at fast growth velocities (up to 40 µm/s here.)
- we can use the confocal mode to reconstruct the 3D solidification microstructures.

Such combinations provide unprecedented insights into the phenomenon investigated here, as we demonstrate below.

3.1. Particle-scale observations

The observation of a partially-frozen structure (Fig. 2) already provides a fresh look at the organization of particles and the late stages of freezing. Elongated regions of concentrated particles, typically encountered in ice-templated materials, can be observed between the crystals. The directionality of growth induced a directional segregation pattern.

If most of the particle reorganization took place here between adjacent ice crystals, some of the particles were also segregated between the crystal and the lower glass slide, resulting in the particle monolayer regions seen for instance in the insets B and C of Fig. 2. Although this is just a boundary limit effect, it provides an ideal configuration to investigate the penetration of ice in the dense packing of particles. Several configurations, highlighted by the different insets can be observed. In inset A, isolated particles were engulfed by the growing crystals. We could not find evidence of a liquid film around these particles. Although a premelted film is probably still present [24,25], its expected thickness (a few nm) makes it too small to be observable by confocal microscopy. Inset B shows a partially frozen region. Local defects in particle packing can be observed, resulting in pores of different sizes between the particles. The pores between closely packed particles still contain liquid water (as seen by the fluorescence of the dye), while the water in the larger pores is frozen (no fluorescence visible anymore). This observation can be explained by the Gibbs-Thomson depression of the freezing point. The ice entry temperature is lower as the pore size diminishes [26,27]. In inset C, which corresponds to a region at a lower