In Situ X-Ray Radiography and Tomography Observations of the Solidification of Aqueous Alumina Particles Suspensions. Part II: Steady State

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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 focused 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 μm/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.

I. Introduction

The behavior of a solidification front in a suspension of particles is of major interest for its implications in a very large number of theoretical and practical issues. If the physical mechanisms controlling the interactions are relatively well understood for single large particles, the solidification behavior of colloidal suspensions is a matter of great interest, but highly challenging. Conclusions derived from single large particles experiments1–6 cannot be extrapolated to smaller particles (<1 μm) where Brownian motion is dominating and segregation effects are negligible. The analysis is further complicated by the necessity to take into account the various interactions between particles, which could be of different natures: electrostatic, Van der Waals, steric, etc. Additional deviations from the ideal situation such as the distribution of particle size, their surface state, charge, and roughness, could have a major influence over the general behavior and stability of the system but are difficult to take into account. It has been shown previously that during steady state, particles are repelled by the propagating interface and are concentrated between the growing crystals. Particle concentration increases up to the breakthrough concentration, where the interface moves into the interparticle space. This situation corresponds to the propagation of a solidification interface in a porous medium and has been greatly investigated, both theoretically and experimentally.5,6 A common conclusion to all the existing studies of such systems is the existence of a critical interface velocity (or correspondingly a critical particle size for a given velocity) above which particles are engulfed by the moving interface before the maximum particle concentration can be reached.

We focus here on the behavior of an interface propagating in a steady state (in terms of velocity), in a concentrated suspension of colloidal particles where the particle size is relatively large (0.2–3.4 μm) in comparison with the typical colloidal systems (<0.1 μm), but smaller than previous studies (>1 μm), and the interface velocity is relatively large too (>20 μm/s). This corresponds to what is encountered during the processing of porous materials by the freeze-casting process.7,8 Under these conditions, diffusion cannot a priori take place, the interface velocity being too high, and the particle redistribution is obtained by the direct interaction with the solidifying interface, which considerably simplify the analysis. The growth kinetics were directly measured—although the in-plane growth anisotropy between the a and c axis was not accessible—and several parameters controlling the redistribution of particles were identified, in agreement to those identified in the first companion paper.9

II. Experimental Procedure

All the experimental methods have been described in the first companion paper, “In situ X-ray radiography and tomography observations of the solidification of aqueous alumina suspensions, Part I: Initial Stages.”10 In the present part, additional powders were also used; their characteristics are given in Table I. The steady state regime observations were performed in a region 4–6 mm from the nucleation surface the powders were obtained through Taimei (Taimei Chemicals, Tokyo, Japan), Sasol (Sasol North America Inc., Tucson, AZ) and Almatis (Almatis, Leetsdale, PA).

III. Results

(1) Steady-State Solidification

Images of the steady state solidification regime of the 1.3 μm particles suspension, obtained by radiography, are shown in

Table I. Characteristics of Powders Used in this Study

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Product name</th>
<th>D₉₀ (μm)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taiimei</td>
<td>TM DAR</td>
<td>0.2</td>
<td>14.5</td>
</tr>
<tr>
<td>Sasol</td>
<td>Ceralox SPA 0.5</td>
<td>0.4</td>
<td>8</td>
</tr>
<tr>
<td>Almatis</td>
<td>CT1200SG</td>
<td>1.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Almatis</td>
<td>CT800SG</td>
<td>3.4</td>
<td>1</td>
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Fig. 1. Solidification sequence in the steady-state, radiography, 1.3 μm particles. Time picture was taken: a = t₀, b = t₀+6 s, c = t₀+13.7 s, d = t₀+22.3 s, e = t₀+27.3 s, and f = t₀+34.7 s. Scale bar: 500 μm.

Fig. 2. Interface location (◇) and velocity (▲, dashed line: running average, window width of 11 points, excluding points A and B) versus time, steady state, 1.3 μm particles. The running average velocity of the interface is decreasing from 39 to 36 μm/s. The z = 0 position corresponds to the position of the interface in Fig. 1(a) (time t₀). The velocities peaks noted A and B are significant, but will be discussed in a separate paper.

Fig. 3. Radiographs of the ice and particle rich phases, showing the interface location (◇) and the particle distribution. The vertical cross section reveals the arrangement of the ice crystals in the direction perpendicular to the solidification direction. The corresponding horizontal cross sections shown in Figs. 3(b)–(e) reveal the arrangement of the ice crystals in the direction perpendicular to the solidification direction. Crystals are lamellar, as discussed previously, but arranged in domains with similar orientations (Figs. 3(f)–(i)). The orientation of each domain can be related to the original nucleation conditions, as discussed in the previous paper. The arrangement of the domains is retained over large distances, as seen on the sequence of cross sections. The displacement of the domains boundaries can be partially explained by the small tilt of the crystals (a few degrees, visible in Fig. 3(a)).

Quantitative information can be extracted from these images, so that the particle rich phase fraction (as discussed previously) can be plotted versus the position of the interface (Fig. 5), along with the corresponding interface velocity obtained through the radiography data. The interface velocity is slowly decreasing, but the particle fraction is constant, within the measurement error range (estimated at 0.5%). The particle fraction is not dependent on the interface velocity under these solidification conditions. Using the horizontal cross sections, the structural wavelength of the frozen structure can be measured; this parameter corresponds to the average crystals+entrapped particles length measured perpendicular to the c-axis of the crystals, as measured before. The structural wavelength decreases from 41 to 35 μm when the interface velocity increases (Fig. 6), as was shown before in such systems. We nevertheless have here a direct and local measurement of this relationship, which is not the case when measured after sublimation and sintering, with the corresponding shrinkage accompanying densification.

(2) High-Resolution Observations

High-resolution observations were performed on the same systems (0.4 μm particles) with the same temperature conditions, to provide direct observations of the crystals growth, and particles displacement. Such a sequence shown in Fig. 7 confirms the lamellar morphology of the ice crystals, as reported previously. The liquid–solid transformation of water into ice is accompanied by a 4 vol.% increase, which leads to a displacement of the suspension ahead of the ice crystals. A detail is shown in Fig. 8, where the tip of the ice crystals can be seen more clearly, just emerging from the concentrated particles zone. It is evident that under these conditions the particles are not concentrated ahead of the tip of the crystals, but in-between the crystals. Similar observations with larger particles (3.4 μm particles) were performed, to investigate the influence of particle size. The sequence is shown in Fig. 9. A similar behavior is observed, with one noticeable difference: the presence of a concentrated particles zone ahead of the interface. The crystals tips are not emerging from this concentrated zone. In addition, the height of this concentration zone is increasing as the interface is advancing. Segregation of the particles can also be observed with particles progressively falling toward the bottom of the suspension; which is not surprising considering the relatively large size of the particles.
The position of the interface and its velocity measured from these observations are plotted in Fig. 10, for the two types of particles (0.4 and 3.4 μm). As shown before (Figs. 4 and 5), the interface velocity is slowly decreasing with time, from 24 to 17 and 12 μm/s, respectively, for small and large particles (faster decrease for larger particles). The absolute velocity values cannot be compared with Figs. 4 and 5, as observations were performed at a different vertical position of the samples. As the interface velocity is progressively diminishing along the vertical direction, observations performed further away from the cold surface will reveal lower interface velocities.

IV. Discussion

(1) Crystals Growth

The observed lamellar porous morphology is an indication of the lamellar shape for the ice crystals, in good agreement with the strong anisotropy of growth kinetics of the $a$- and $c$-axes of hexagonal ice. The particles arrangement can nevertheless be expected to be affected by the high-temperature densification step (sintering). Such lamellar morphology is clearly evident in the 2D observations in Fig. 7 and in 3D observations in Fig. 11. Growth behaviors usually associated with dendritic growth,
such as tip splitting and side branch instability, are also observed here (arrows in Fig. 4(a)). Such side branch instabilities do not lead to creation of neighboring primary dendrites because by the time such protruding dendrites turn into stable dendrites growing along the $z$-axis, the surrounding crystals have already grown, resulting in the increase of the concentration of particles ahead of the newly created dendrites. Because the remaining space available for their growth is limited; they terminate, either by stopping halfway in between the lamellar crystals (Fig. 12(a)), or by reaching the next adjacent crystals (Fig. 12(b)).

The three growth velocities schematically shown in Fig. 13 can be determined from the radiographic sequences, where the evolution of the crystals and particle redistribution below the interface is visible. The $V_{cxy}$ and $V_{axy}$, respectively, correspond to the growth velocities along the $c$- and $x$-axes, in the $xy$ plane, while $V_{az}$ corresponds to the growth velocity along the $a$-axis perpendicular to the $xy$ plane. Using the crystals dimensions on cross sections obtained through tomography, $V_{cxy}$ is estimated to be $14\, \mu m/s$, and the $V_{az}$ about $18\, \mu m/s$ (1.3 $\mu m$ particles). For the smaller $0.4\, \mu m$ particles, $V_{cxy}$ and $V_{az}$ are about 14 and 20 $\mu m/s$, respectively. These observations suggest that growth kinetics along the $a$- and $c$-axes are similar. However, it is important to note here that what we measure is not the actual anisotropy of growth kinetics (defined as $V_{axy}/V_{cxy}$), because the growth rate measured in the $z$-direction is influenced by the temperature gradient, which is not the case for the growth in
the x or y direction (Fig. 13). To access the anisotropy of growth kinetics, one should measure $V_{ax,y}$ and $V_{cxy}$, where the temperature conditions are homogeneous, so that the measured growth rates are not dependent on the temperature gradient. Such measurement cannot be performed with these types of experiments, until full-tomography acquisitions can be performed within a much shorter time to obtain in situ 3D evolution of the crystals growth.

(2) Particle Redistribution

From the various observations shown here, it appears that redistribution of particles in front of the advancing interface is dependent on several variables. First, particle redistribution depends on the interface velocity. This dependency seems rather obvious, and could be understood when interpreting the system in terms of colloidal particles and diffusion. However, at larger interface speeds the particles cannot migrate by Brownian diffusion, so that the problem cannot be treated in terms of diffusion.

Particles are directly repelled by the moving solidification front. For moderate to slow velocities (1 μm/s), enough time is available for the particles to migrate by Brownian diffusion, so that a layer of concentrated particles can build up ahead of the interface. This situation has already been deeply investigated. In such case, the concentration of particles ahead of the interface can potentially lead to a situation of constitutional supercooling, where ice crystals will be able to nucleate within the concentrated zone, leading to a different morphology of particles arrangement in the solidified body. Under the temperature conditions typically used, it is quite clear that the diffusion approach cannot be used to determine the concentration profile and particle redistribution behavior in this case.

Particle redistribution also depends on the ratio of particle size and intercrystals spacing. Although the relationship between particle size and diffusion is quite clear (see, e.g., Fig. 3 in Peppin et al.17), additional effects are associated to the particle size, under conditions where no diffusion is possible. As shown in Figs. 7 and 9, a zone of concentrated particles builds up when larger particles are used, a situation that cannot be explained through diffusion because this mechanism is less likely to occur as particle size is increasing. It is proposed here that this increase in the concentration ahead of the interface may be due to the fact that the larger particles of sizes approaching crystal sep-

**Fig. 8.** Detail of the solidification sequence in the steady state (Fig. 7), high-resolution radiography. 0.4 μm particles. Details of the dendrites tip. No visible concentration of particles ahead of the dendrites tip is observed. Interface velocity: 20 μm/s. Scale bar: 50 μm. Arrows indicate the dendrites tip. The solidification front is moving vertically, bottom to top.

**Fig. 9.** Solidification sequence in the steady state, high resolution, 3.4 μm particles. Time picture was taken: $a = t_0$, $b = t_0 + 4$ s, $c = t_0 + 9.7$ s, $d = t_0 + 16$ s, $e = t_0 + 24.7$ s. Scale bar: 150 μm.

**Fig. 10.** Interface position and velocity from high resolution observations, for 0.4 μm (△) and 3.4 μm (○) particles.
ration distances cannot be accommodated between the primary dendrites, as mentioned and schematically illustrated in Fig. 8 in the companion paper. The presence of a concentrated particles zone can affect the growth of the ice crystals, their growth kinetics was found to slow down faster when concentrated particles were present (Fig. 10).

Finally, particle redistribution depends on the shape and the orientation relationship between the crystals and the temperature gradient direction. This has been shown for the first instants of solidification in the companion paper, and is confirmed here in steady state. The redistribution of particles in directions parallel and perpendicular to the interface displacement direction is not dictated by diffusion, as discussed previously, but rather by the orientation of the growing crystals and the efficiency of particles packing when the particles concentration is increasing between the moving interfaces. As a consequence, one should refer to this situation as a metastable steady state, dictated by the applied temperature conditions (cooling rate). Providing that the crystals orientation is constant and the intercrystals distance large enough (compared with the particle size), particle redistribution occurs homogeneously in the xy plane (with a constant packing efficiency, as defined in the companion paper) and does not occur in the z direction. The fraction of entrapped particles is therefore constant, resulting in homogeneous materials after removal of the solvent.

V. Conclusions

Based on in situ experiments by X-ray radiography and tomography of the controlled solidification of concentrated alumina particles aqueous suspensions, the following conclusions can be drawn, regarding the steady-state regime (in terms of velocity).

Because of the relatively rapid interface velocities (20–40 μm/s), particle redistribution cannot occur laterally by Brownian diffusion.

Particle redistribution in the solidification plane is obtained through direct interactions with the solidification front, particles being pushed by the moving interface. The critical parameters to be considered here are therefore the orientation of the growing crystals and the efficiency of particles packing when the particle concentration increases between the moving interfaces, efficiency directly related to the particle size and intercrystals spacing.

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References


Fig. 11. Three-dimensional representation of an isolated lamellar crystal, 1.3 μm particles. Perspective (a), side (b), and top view (c). Crystal height represented: 360 μm. The surface of the crystal is not faceted.

Fig. 12. Growth termination of dendrites, three-dimensional representation. Black arrows indicate the origin of the dendrites and white arrows their termination. The dendrites can either stop in between the crystals (a), or reach the next adjacent crystal (b).

Fig. 13. Growth velocities and crystal orientation. Ice, under these conditions of temperature and pressure, is hexagonal with strong anisotropies of interface kinetics between the a- and c-axes, resulting in platelets-like crystals.


