Experimental and numerical investigations of NH_4Cl solidification in a mould

Part 1: Experimental results

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This work represents a benchmark experiment to test numerical solidification codes dealing with combined columnar and equiaxed growth. The solidification of a hyper-eutectic NH_4Cl–H_2O solution has been investigated in a $100 \times 80 \times 10$ mm^3 brass cell cooled on three sides from 41°C down to 26°C. The cell was illuminated by a laser generated light sheet and images were recorded throughout the whole solidification process. Both columnar and equiaxed growth of NH_4Cl was observed. The freckle formation observed during preceding experiments in a $100 \times 100 \times 30$ mm^3 brass cell was not present in this thinner cell which made the cell more suitable for comparison with numerical predictions. Numerical simulations of the same solidification process were performed using an Eulerian-Eulerian multiphase approach and its details will be presented in Part 2.

Keywords: NH_4Cl solidification, multiphase flow, convection, numerical simulation

Introduction

Amongst other phenomena, simultaneous liquid flow and solid movement is an important phenomenon in solidification.[1] Convection in the liquid melt is mainly caused by thermo-solutal buoyancy forces, while the movement of free solid crystals is due to the density difference of solid and liquid under the influence of gravity.

The two phase model proposed by Ludwig *et al*. has been thought to be able to describe globular equiaxed solidification and the Columnar-to-Exquiaxed Transition (CET).[2–8] Whether such an Eulerian multiphase model will describe solidification and phase separation processes properly, is strongly dependent on the definition and implementation of source terms, interaction terms, and other auxiliary terms for the corresponding conservation equations. Thus, experiments with well defined boundary conditions are essential to verify such numerical predictions.

An important contribution to this field was done by Beckermann *et al*.[9–11] where both numerical and experimental results for NH_4Cl solidification proved the suitability and limits of the applied numerical solidification model. The aim of the present investigation is to create benchmark experiments which can be used to validate numerical models for both columnar and equiaxed solidification. In a previous investigation,[12] the authors presented results by using Particle Image Velocimetry (PIV) in order to measure the natural convection of water in a die cast model. In this work the same technique is used to visualize the solidification process.

Experimental technique and setup

The experimental cell is a square cavity with $10 \times 10 \times 1$ cm^3. The two side walls and the bottom are made from brass and the front and back sides are made from glass plates.[12] A meander path for the cooling liquid through the bronze walls generated a homogeneous cooling. The cooling was done with a HAAKE C30P bath linked through silicone tubes to the cell walls. The coolant liquid was a mixture of water and ethanol, which can be used as coolant down to −35°C. The temperature in the cell walls was monitored via thermocouples. NiCr-Ni thermocouples (accuracy +/−0·1°C) were connected to a thermocouple reader (Stanford SR 630), which continuously recorded the temperature during the experiment and linked the image acquisition with the temperature through a trigger signal. A double cavity Nd-YAG laser (frequency doubled, λ=532 nm) was used as a light source. In contrast to the shadowgraph technique applied by Beckermann *et al*.[9–11] the presented PIV setup generated a 2 mm wide light sheet that illuminated the cell from the top. Thus, the PIV setup results represent a quasi two dimensional cross section of the solidification process, whereas the shadowgraph technique generated volume averaged results. The image acquisition was performed with a CCD camera mounted perpendicularly to the cell. Pictures were evaluated using the

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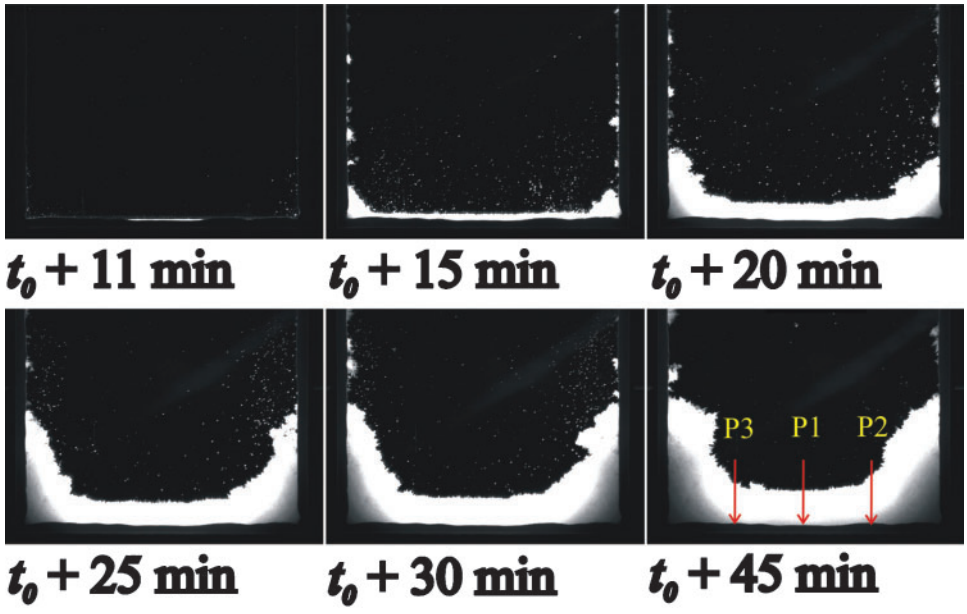


1 Sequential images of the 29·5 wt-% NH_4Cl-H_20 solidification process in a 10 cm wide mould

commercial software 'Flow Manager', developed by Dantec Dynamics.[13] The camera lens was covered with a band pass filter $\lambda = 532 \pm 3$ nm, to ensure that the CCD camera only recorded direct or scattered light from the laser source and excluded background light.

Measurement procedure

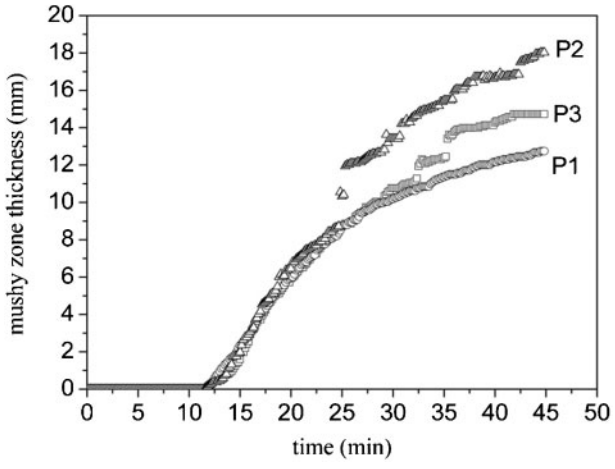
In the present experiments a hypereutectic alloy of 29·5 wt-% NH_4Cl was solidified. According to the phase diagram published in ref,[1] the liquidus temperature for this concentration is 36°C. The solution was prepared at 41°C and then poured into the cell that had been preheated at 41°C. The height of the solution in the cell is 8 cm. Next, the solution rested for 15 minutes. After this holding time, the cooling of the cell walls was started at time t_{initial} by setting the bath to 26°C. The temperature was recorded by the thermocouples fixed in the cell walls. The resulting temperature profile was similar to the one published elsewhere,[12] i.e. a linear cooling rate of 1·2 °C min^{-1} was observed for the first 826 sec until the set temperature was reached and then the temperature stayed at $26° \pm 0{\cdot}1$°C for the rest of the process. Note that this temperature is only sufficient to solidify around 20% of the sample. The recording of the images started simultaneously with the cooling of the cell walls at $t_{initial}$; images were taken every 10 seconds until the solidification was complete, i.e. ~45 minutes after $t_{initial}$.

Results and discussion

Figure 1 shows sequential images of the solidification process together with the time at which the images were taken. In the first stage of the solidification process (image not shown) a convection of the melt was observed with a downward flow near the cell walls and an upward flow in the centre. This can be understood as the thermal convection, caused by the temperature dependent density of the melt. In the second stage of the solidification process, columnar dendrites were observed growing from the sidewalls approx. 11 minutes (700s) after t_{initial}. In the third stage a large number of equiaxed grains appeared in the lower part of mould where according to previously published measurements[1] the temperature had dropped below the liquidus temperature. Notice that according to additional experiments intended to capture both the crystal movement and the movement of the melt (not shown) the thermal convection pattern at this stage of solidification was replaced by an unsteady flow pattern. This can be explained by the increasing influence of solutal convection that opposes the thermal convection at this stage. In the following stages of the solidification process, the equiaxed grains followed the convectional flow and some of them interacted with columnar crystals at the side walls where they were captured. These captured grains grew together with the columnar dendrites towards to the melt. Other equiaxed grains were rejected from the sidewalls into the bulk melt by the thermal and solutal convection driven flow. These crystals continuously grew until they reached a size where gravity dominated over the other forces, thus they settled to the bottom of the mould. The solidification process ended 34 min after the first crystals had appeared, i.e. 45 minutes after t_{initial}. At the end of the process around 35% of the cavity is covered with mush.

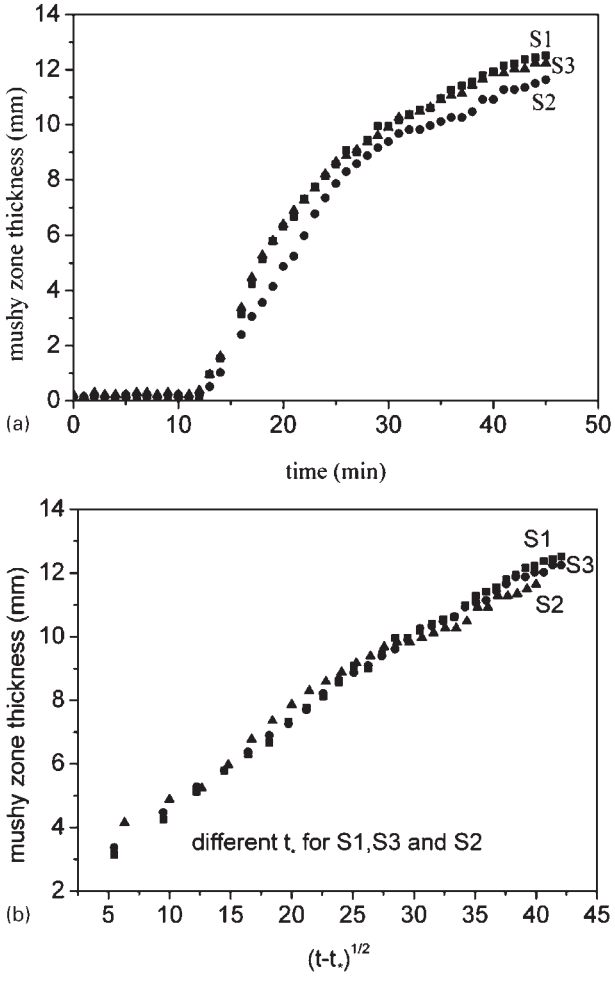
A measurement of the mushy zone thickness at the vertical walls was hindered by the fact that it was frequently observed that the mixed equiaxed/columnar NH_4Cl growing horizontally from the side walls broke due to gravity and the strong flow along the walls. The first breaks of the horizontally growing crystals were usually observed 25 minutes after t_{initial}. On the other hand the horizontal solid layer at the bottom grew homogeneously throughout the process. To monitor the growth of the mushy zone, its thickness was therefore measured at three different positions perpendicular to the bottom cell wall. The three positions are indicated in the last image in Figure 1.

Figure 2 shows a plot of the mushy zone thickness versus the solidification time at these three different positions. The jumps in the measured thickness at P2 and P3, i.e. the two positions at 2·5 cm distance from the cell walls, indicate that crystals had broken off the

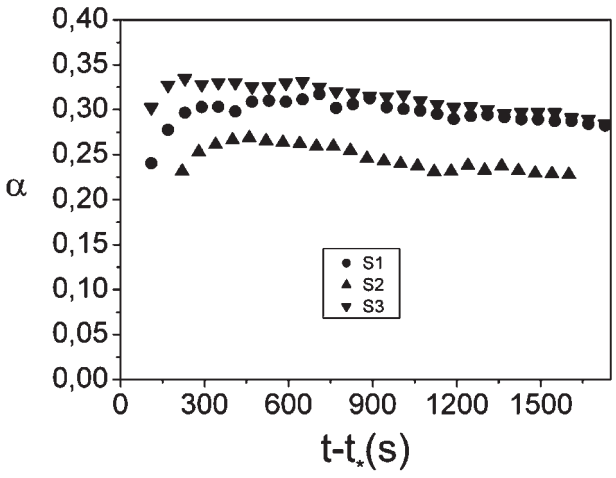


2 Measured thickness of the columnar zone at three positions on the bottom wall as indicated in the last image of Fig. 1

vertical walls and settled on top of the solid layer growing from the bottom. However, the thickness measured in the centre of the cell, i.e. at P1, showed a



3 *a* Measured thickness of the columnar zone in the centre of the bottom wall versus time for three different experiments with the same initial concentration (29·5 wt-% NH_4Cl) and cooling rate; *b* Measured thickness of the columnar zone in the centre of the bottom wall versus $\sqrt{t-t_*}$ for three different experiments with the same initial concentration (29·5 wt-% NH_4Cl) and cooling rate



4 Evolution of $\alpha_{\sqrt{t}}$ (definition given in the text) for the three experiments presented in Fig. 3

continuously increasing layer. Figure 3a shows the corresponding centre position measurements for 3 different experiments with the same initial concentration and the same cooling rate. The plot indicates that t_0 (the time when solidification started) and the thickness of the mushy zone at P1 at certain times of the solidification process were reproducible within 10% of the measured thickness. Figure 3b shows the mushy zone thickness measured at P1 plotted versus $\sqrt{t-t_*}$.

On these plots of mushy zone thickness versus time, two growth regimes were observed. Initially the amount solidified increases linearly with time, later the amount solidified increases linearly with the square root of time[14] as shown in Figure 3b. The square root of time growth regime can be described by the following equation:

$$d=\alpha\sqrt{(t-t_*)}+\beta \quad (1)$$

where d is the thickness of the mushy zone; t the solidification time, t_* the time when the square root of time growth period starts and β the thickness of the mushy zone at t_*.

α was calculated for each point in the linear and in the square root of time regime, as $\alpha_{\text{lin}}=\dfrac{d}{t-t_0}$ and $\alpha_{\sqrt{t}}=\dfrac{d-\beta}{\sqrt{(t-t_*)}}$, respectively. Figure 4 shows plots of $\alpha_{\sqrt{t}}$ versus the solidification time. At the beginning of 'the square root of t' growth regime, $\alpha_{\sqrt{t}}$ is not constant but after a very short time becomes approximately constant. Nevertheless, a little decrease in $\alpha_{\sqrt{t}}$ was noticed. The magnitude of the $\alpha_{\sqrt{t}}$ factor is related to the local thermal and solutal gradient at the solidification front. The observed decrease of $\alpha_{\sqrt{t}}$ can therefore be attributed to the fact that both gradients decrease with solidification time. Table 1 shows the calculated average α factors for the three experiments presented in

Table 1 Average α-factors for the three experiments presented in Fig. 3

	α_{lin}	$\alpha_{\sqrt{t}}$
S1	0·01096	0·29
S2	0·01071	0·23
S3	0·01039	0·30

Fig. 3. The average values of the α-factors show only small variations between the different experiments and are therefore considered suitable as a parameter to validate the numerical calculations of the solidification process.

Summary

This work represents benchmark experiments with NH_4Cl–H_2O solutions designed to test numerical solidification codes dealing with combined columnar and equiaxed growth. It has been shown that several experiments with a fixed geometry, initial concentration and cooling rate generated reproducible results. Furthermore the various stages of the solidification process that have to be reproduced by numerical models were shown. For a quantitative comparison with numerical results, the thickness of the mushy zone at certain positions in the setup was monitored versus the solidification time. The resulting plot was fitted with a function following the square root of time law and the reproducibility of the implemented α-factor was demonstrated. In the second part of this work[6] the presented experimental results are compared with numerical simulation predictions gained by a sophisticated Eulerian-Eulerian multiphase approach.

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