Experimental and numerical investigations of NH_4Cl solidification in a mould

Part 2: numerical results

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This paper deals with the validation of a multiphase solidification model based on a benchmark experiment presented in Part 1. For the numerical modelling of NH_4Cl–H_2O solidification, the three different phases liquid, columnar dendrite trunks and equiaxed grains have been considered. The mass, momentum, energy conservation and species transport equations for each phase have been solved. The multiphase Eulerian-Eulerian model equations have been implemented in the Finite Volume Method based commercial software FLUENT-ANSYS using User-Defined Functions (UDF). The simulation of the NH_4Cl–H_2O solidification has been numerically investigated as a two-dimensional unsteady process representing a cross-section of a $100 \times 80 \times 10$ mm experimental benchmark. During the experiment both columnar and equiaxed growth of NH_4Cl were observed, therefore both phenomena were considered in the simulation. The predicted distribution of the solidification front has been compared with the measurements.

Keywords: Multiphase flow, Numerical methods, NH_4Cl-H_2O solidification

Introduction

The numerical investigation of NH_4Cl–H_2O solidification is a relevant opportunity to validate a model set up for the phenomena with experimental data.[1] The experimental validation of a multiphase model using a NH_4Cl–H_2O transparent model alloy for equiaxed dendritic solidification was studied by Wang and Beckermann.[2–4] The present paper uses a volume averaged multiphase model by Ludwig *et al.*[5] and Wu *et al.*[6,7] considering both columnar and equiaxed growth which were observed during the NH_4Cl solidification process. The mass transfer has been modelled by diffusion controlled crystal growth. A hexagonal arrangement of the dendrite trunks has been assumed to compute the mass transfer of columnar growth. The results were compared with measurement where the measurement cell was illuminated by a laser light sheet and digital images were recorded during the whole solidification process.[1]

Brief description of the model

A multiphase solidification model was developed for the binary system NH_4Cl–H_2O. The most relevant simulation parameters are given in Table 1, more data can be found in previous work by Wang and Beckerman.[2–4]

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Three phases were considered, namely liquid phase l, columnar dendrite trunks c and equiaxed grains e. The morphology of the equiaxed grains was approximated by ideal spheres. The columnar dendrite morphology was approximated by step-wise growing cylinders with constant primary arm spacing. The growth velocity of columnar dendrite trunks and equiaxed grains were analytically derived.[5–7] The mass transfer rate from the columnar to the equiaxed phase was neglected. The momentum equation for the columnar phase was not solved, because the dendrite tip was tracked by an explicit type algorithm using the Lipton-Glicksman-Kurz (LGK) model.[8] A hexagonal arrangement of the dendrite trunks has been assumed to compute the mass transfer between liquid and columnar phase.[9] The Gibbs-Thomson coefficient Γ of the tip velocity expression is an important parameter of the simulation process that strongly influences the final distribution of the dendritic structure. Since there were no measurements available to predict this growth kinetic parameter, it was adjusted by computational experience. Thermal and solutal buoyancy were modelled by using the Boussinesq approach. The nucleation process was modelled by the Oldfield[10] conservation equation which suggests a continuous rather than a discrete distribution of nucleation sites. The nucleation process has been described by the conservation of the number density n of equiaxed grains in the numerical model. Due to the fact that the nucleation parametes, $n_{\max}$, ΔT_N and ΔT_σ were not known exactly, their values were adjusted by the results of the Particle Image Velocimetry (PIV) as optical measurement method (see their values in

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Table 1). The authors performed a parameter study and nucleation parameters were varied according to different experiments.

After computing the mass transfer rates, the multiphase Eulerian-Eulerian approach was applied to consider the mass, momentum, enthalpy, species and grain density conservations. The conservation equations for each phase were implemented in the Finite Volume Method based commercial software FLUENT-ANSYS v6·3 by means of User-Defined Functions (UDF). Further details about the multiphase volume averaging model can be found in the literature.[5–7,9]

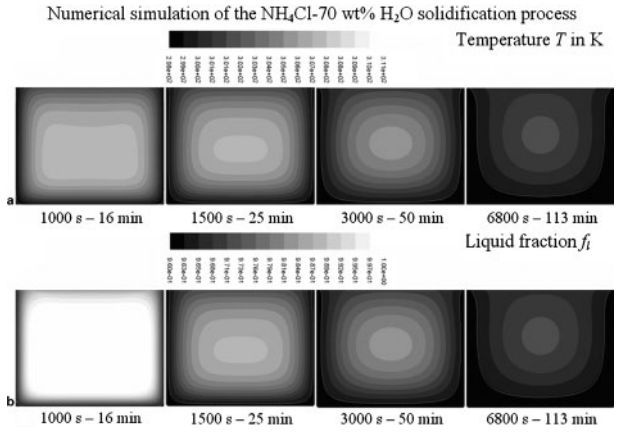
Results and discussion

In this section the numerical results for columnar and equiaxed dendritic solidification of a NH_4Cl–70wt-% H_2O solution are discussed. The distribution of the dendritic structure has been compared with experimental data. The temperature at the wall of the solidification cell $T_W(t)$ was time-dependent. Temperature measurements during the solidification experiments showed a cooling rate at the side and bottom walls of the mould that could be approximated by the following function:

$$T_W(t) = 314{\cdot}70325 - 0{\cdot}02019t \quad (1)$$

where t is the time in seconds. This approximated function was used until $t \leqslant 826$ s and after that the measured temperature was constant at 298 K.[1] Air flow, i.e. a free slip condition, was assumed as boundary at the top, no slip was assumed at the side and bottom walls. Due to the cell dimensions and the good thermal isolation of the glass plates a 2D simulation was considered adequate to model the solidification process. A square grid consisting of 40×80 cells was chosen with a vertical symmetry axis, thus only half of the symmetrical domain had to be computed. The width and the height of the 4000 cells were 1 mm. The computational time was approx. 3 days and the solution converged well with a time step size of 0·1 s.

The numerical model considered columnar growth, nucleation and growth of equiaxed grains, motion and sedimentation of grains, solute transport by diffusion and convection. The fragmentation and attachment of crystals were neglected. Figure 1 shows a series of simulation results at various stages of the NH_4Cl-70 wt-% H_2O solidification process; Figure 1a) gives a comparison of the temperature fields that were always plotted with the same range, i.e. from 298 K to 311 K in



1 Numerical simulation of the NH_4Cl-70 wt-% H_2O solidification process; a) Temperatures from 298 K to 311 K in 15 levels of grey with a superimposed white isoline for liquid fraction f_l=96·6 wt-%; b) Liquid fraction f_l from 0·96 to 1 in 15 levels of gray with a superimposed white isoline for solid fraction of the equiaxed phase f_e=3·4 wt-%

15 levels of grey. Furthermore, a white isoline was superimposed that represents the liquid fraction f_l=96·6 wt-%. This isoline represents 3·4 wt-% solid fraction f_s whereas Beckermann *et al.*[4] postulated 5 wt-% solid fraction for the NH_4Cl mush. The f_s=3·4 wt-% isoline thus marks the 'solidification front'.

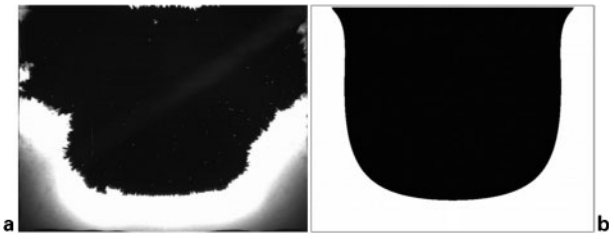
Figure 1b) gives a comparison of the liquid fraction fields, plotted for a fixed range of f_l from 0·96 to 1 in 15 levels of gray. Furthermore these images show a superimposed white isoline for a solid fraction of the equiaxed phase f_e=3·4 wt-% .

1000 s after the start of the process the temperature near the walls had fallen below the liquidus temperature of the initial concentration and columnar growth had started at the side walls and in the bottom corners accompanied by the formation of equiaxed grains in the undercooled liquid. This first stage of solidification was also observed in the experiment.[1]

The evolution of the temperature field shows isothermes with a U-type shape. During the experiment it was observed that the equiaxed grains interacted with columnar crystals and the grains have been captured close to the mould wall. The captured grains grew together with the columnar dendrites towards the melt. Other equiaxed grains were rejected from the sidewalls into the bulk melt by the thermal and solutal convection

Table 1 Data system for simulation of NH_4Cl–70 wt-% H_2O solidification

Cavity dimensions $L \times H$ (cm × cm)	10×8
Data for initial and boundary conditions:	
Initial temperature of the liquid melt, T_{in} (K)	307
Initial concentration, C_{in} (wt-%)	70
Thermal and solutal expansion coefficients:	$3{\cdot}32 \times 10^{-4}$
Thermal expansion coefficient, β_T (K^{-1})	$3{\cdot}65 \times 10^{-4}$
Solutal expansion coefficient, β_C (wt-$\%^{-1}$)	
Nucleation parameters:	
Maximum equiaxed grain density, n_{max} (m^{-3})	10^4
Gaussian distribution width for nucleation law, ΔT_σ (K)	2
Undercooling for maximum grain production rate, ΔT_N (K)	8
Empirical constants:	
Maximum grain packing limit, $f_e^{critical}$	0·637
Initial grain diameter, d_{ei} (μm)	1
Primary dendrite arm spacing, λ_1 (μm)	1



2 The experimentally measured *a* and numerically predicted *b* shape of the mushy zone (white) of NH_4Cl–70 wt-% H_2O at the end of the solidification process (as defined in the text)

driven flow. A downward flow developed due to the cooling effect next to the sidewalls where the thermal buoyancy forces oppose the upward solutal buoyancy forces. The free moving grains continued to grow in the liquid and settle due to the density difference between the solid and liquid phase. This observation was in good agreement with Beckermann *et al.*[11] who also postulated that the curved shape of the sediment structure of the equiaxed grains is largely caused by the thermo-solutal convection in the melt, because the movement of the smallest crystals closely follows the motion of the liquid due to the large interfacial drag.[11]

The numerically predicted liquid fraction isolines in Fig 1a) very closely follow the shape of the isothermes until approx. 110 min. After that time the temperature within the cell still changed but the shape of liquid fraction isolines remained unchanged (images not shown). This time and the unchanging shape of the solidification front were therefore considered as the end of the solidification process. A similar saturation behaviour was observed in the experiment.[1]

A comparison of the f_l=96·6 wt-% liquid fraction line and f_e=3·4 wt-% solid fraction line of the equiaxed phase showed only minor differences throughout the solidification process. Thus the numerical results indicate that the equiaxed growth dominated the NH_4Cl growth process and the columnar growth played a minor role. This was an important result of the simulation because in the experimental observation the two growth modes could not be distinguished.

Figure 2 shows a comparison of the experimental and the numerical model at the end of the solidification process. In the bottom of the solidification cell the calculated thickness and shape of the mushy zone was in good agreement with the experimental result. However, the experiment revealed a break-off phenomenon of the NH_4Cl crystals at the vertical cell walls that had not been taken into account in the numerical model. Therefore the shape of the calculated solidification front did not resemble the experimental shape in that region of the measurement cell. Overall, the numerical simulation based on the proposed multiphase model has produced a qualitatively similar grain distribution in the tested mould to the experiment. The quantitative comparison of the numerically predicted results and the measurements will be discussed in a future publication.[12]

Summary

A multiphase approach has been used to model NH_4Cl–H_2O solidification considering both columnar and equiaxed growth which were observed during the process. The morphology of equiaxed grains was approximated by ideal spheres. The columnar dendrite trunks were assumed to be cylinders. The grain sedimentation and nucleation phenomena were discussed concerning the most important parameters for the nucleation process. The Gibbs-Thomson parameter was adjusted based on the simulation experience. The results show qualitatively good agreement with experimental data for the distribution of the columnar and equiaxed dendritic structure in the bottom part of the mould at the end of the solidification, however it disagreed in the upper part of the mould, because the break-off phenomena had been neglected in the model.

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