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Numerical and Experimental Investigation of NH_4Cl Solidification

L. Könözsy[1,a], M. Stefan Kharicha[2,b], S. Eck[2,c], M. Wu[2,d] and A. Ludwig[1,2,e]

[1] Christian Doppler Laboratory for Multiphase Modelling of Metallurgical Processes, University of Leoben, A-8700 Franz-Josef Str. 18, Leoben, Austria

[2]Department Metallurgy, Chair for Simulation and Modelling of Metallurgical Processes, University of Leoben, A-8700 Franz-Josef Str. 18, Leoben, Austria

[a]laszlo.koenoezsy@mu-leoben.at, [b]mihaela.kharicha@mu-leoben.at, [c]sven.eck@mu-leoben.at, [d]menghuai.wu@mu-leoben.at, [e]andreas.ludwig@mu-leoben.at

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Abstract. This paper deals with the validation of a volume averaged multiphase solidification model based on a benchmark experiment using NH_4Cl-H_2O as model alloy and Particle Image Velocimetry (PIV) as optical measurement method. For the numerical modelling of the solidification, different phases (e.g. liquid, equiaxed grains and columnar dendrite trunks) have been considered. The mass, momentum, energy conservation and species transport equations for each phase have been solved. The Eulerian-Eulerian model equations have been implemented in the commercial Finite Volume Method based software FLUENT-ANSYS v6.3 using User-Defined Functions (UDF). The mass transfer has been modelled by diffusion controlled crystal growth. The simulation of the NH_4Cl-H_2O solidification has been numerically investigated as a two-dimensional unsteady process in the cross-section of a 100 x 80 x 10 (mm^3) experimental benchmark. Since during the experiment both columnar and equiaxed growth of NH_4Cl have been observed, both phenomena have been considered in the simulation. The predicted distribution of the solidification front and the measured thickness of the mushy zone have been compared with the measurements.

Introduction

The liquid flow and solid movement are important phenomena in solidification. Convection in the melt is mainly caused by thermal and solutal buoyancy forces, and the movement of free solid crystals is furthermore influenced by the density difference of solid and liquid combined with gravity. The experimental validation of a two phase multiphase model [1-2] using a NH_4Cl-H_2O transparent model alloy for equiaxed dendritic solidification was studied by Wang and Beckermann [3]. The numerical investigation of NH_4Cl-H_2O solidification is a relevant opportunity to validate a volume averaged multiphase model by Ludwig et al. and Wu et al. [4-6]. The present study deals with both columnar and equiaxed growth which were observed during the NH_4Cl solidification process. The results have been compared with measurements using Particle Image Velocimetry (PIV) as optical method. The authors presented this technique to measure the natural convection of water in a die cast model [7].

Brief description of the multiphase Eulerian-Eulerian model

A volume averaged Eulerian-Eulerian multiphase solidification model was developed for the binary system NH_4Cl-H_20. Three phases are 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 growth velocities of equiaxed grains were analytically derived [4-6] as

$$v_{R_e} = \frac{2D_l}{d_e} \cdot \frac{c_l^* - c_l}{c_l^* - c_e^*}, \tag{1}$$

where D_l is the diffusion coefficient, d_e is the diameter of the equiaxed grains, c_l^* and c_e^* are the equilibrium species mass fractions at the liquid/solid interface. The columnar dendrite morphology was approximated by step-wise growing cylinders with constant primary arm spacing λ_1 (see Table 1). The momentum equation for the columnar phase was not solved, because the dendrite tips were tracked by an explicit type algorithm using the LGK [8] model. The growth velocity of columnar dendrite trunks was analytically derived [4-6] as

$$v_{R_c} = \frac{2D_l}{d_c} \cdot \frac{c_l^* - c_l}{c_l^* - c_c^*} \cdot \ln^{-1}\left(\frac{d_{\max}}{d_c}\right), \tag{2}$$

where $d_{\max}$ is the maximal diameter available for cylindrical growth, d_c is the diameter of columnar dendrite trunks, and c_c^* is the equilibrium mass fraction of the columnar solid at the liquid-solid interface. Considering a hexagonal dendrite arrangement with primary dendrite arm spacing λ_1, the maximal diameter can be chosen as $d_{\max} = 1.05 \cdot \lambda_1$. The mass transfer rate from the liquid to the equiaxed phase was defined as

$$M_{le} = v_{R_e} \cdot \left(n \cdot \pi \cdot d_e^2\right) \cdot \rho_e \cdot f_{imp}, \tag{3}$$

where ρ_e is the density of the equiaxed phase, f_{imp} is the impingement factor [9]. The mass transfer rate from the liquid to columnar phase was defined as

$$M_{lc} = v_{R_c} \cdot \left(\frac{2\sqrt{3} \cdot \pi \cdot d_c}{3\lambda_1^2}\right) \cdot \rho_c \cdot f_{imp}, \tag{4}$$

where ρ_c is the density of the columnar phase, V_{tip} is the tip velocity, and R_{tip} is the tip radius. The impingement factors are different for the spherical and cylindrical growth. An Avrami-type impingement factor was used ($f_{imp} = f_l$) for equiaxed solidification. The impingement factor for columnar solidification was assumed as

$$f_{imp} = \begin{cases} 1, & 0 < d_c \le \lambda_1, \\ 1 - \dfrac{d_c - \lambda_1}{d_{\max} - \lambda_1}, & \lambda_1 < d_c \le d_{\max}. \end{cases} \tag{5}$$

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. After computing the mass transfer rates, the multiphase Eulerian-Eulerian approach is applied to consider the mass, momentum, enthalpy, species and grain density conservations. The conservation equations for each phase were implemented in the FLUENT-ANSYS v6.3 software using User-Defined Functions (UDF). Further details about the multiphase volume averaging model can be found in the literature [4-6].

Experimental setup and measurement technique

The experimental cell is a square with 100 x 80 x 10 (mm^3), the two side walls and the bottom are made of brass and the front and back sides are made of glass plates [11]. A sinusoidal path of 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 automotive anti-freeze, which can cover a temperature range down to -35 (°C). The temperature in the cell walls was monitored via thermocouples. The NiCr-Ni thermocouples (type K) 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. [12] 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 with the help of the commercial software "Flow Manager", developed by Dantec Dynamics [13]. The camera lens was covered with a band pass filter λ=532 +/-3 (nm), in this way the CCD camera only recorded direct or scattered light from the laser source and excluded background light.

Results and discussion

The numerical and experimental results for columnar and equiaxed dendritic solidification of a NH_4Cl-70wt.% H_2O solution are discussed in this section. The cooling rate was measured by thermocouples at the side and bottom walls of the mould and showed a function that could be approximated by the following function:

$$T_W(t) = 314.70325 - 0.02019 \cdot t\,, \tag{6}$$

where t is the time. Thus, $T_W(t)$ is the time-dependent wall temperature based on temperature measurements during the solidification experiments. This approximating function was used until $t \le 826\,(\mathrm{s})$ and after that the temperature was constant at 298 (K). A hyper eutectic alloy of 29.5 (wt.%) NH_4Cl was solidified in the experiment. According to the equilibrium phase diagram, the liquidus temperature for this concentration is 36 (°C). The solution was prepared at 41 (°C) and then poured in the cell that had been held at 41 (°C), until it filled the cell up to 8 (cm). The solution rested for 15 minutes. After this settling time the cooling of the cell walls was started at t_0 by setting the bath to 26 (°C). The recording of the images started simultaneously with the cooling of the cell walls at t_0. The images were taken every 10 seconds until the solidification was completed, i.e. ~45 minutes after t_0. Images of the various stages of the solidification process have recently been published [14].

For the computations, 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. 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 simulated. The width and the height of the 4000 cells were 1 (mm). The computational time for this grid was approximately 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. The most important simulation parameters can be found in Table 1.

According to our experimental observations, the first stage of the process was a counter-clockwise natural convection of the melt in the left hand side of the mould. Columnar dendrites were observed at the early stage of the solidification growing from the sidewalls. Next, equiaxed grains were forming in the bulk melt. These equiaxed grains partially interacted with columnar crystals and some of them have been captured close to the mould wall. The 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. 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 continue to grow in the liquid and settle due to the density difference between the solid and liquid phase. 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 parameters, $n_{\max}$, ΔT_N and ΔT_σ are not known exactly, their values were adjusted by the results of the PIV measurement (see Table 1). The grains finally settled in the bottom of the test mould. The results showed relatively low solid fraction throughout the settling process which was in agreement with previous work by Beckermann et al. [3].

Table 1. *Thermophysical Properties and System Data for NH_4Cl-70 wt.% H_2O Alloy*

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
Material properties:	
Density of the liquid, equiaxed and columnar phases, ρ_l, ρ_e, ρ_c (kgm-3)	1078
Density of the equiaxed phase in the buoyancy term $\Delta\rho$ (kgm-3)	1527
Dynamic viscosity of the liquid phase, μ_l (Nsm-2)	0.0013
Thermal conductivity of the liquid phase, k_l (Wm-1K-1)	0.468
Thermal conductivity of the equiaxed and columnar phase, k_e, k_c	2.7
Specific heat of the liquid phase, c_l (Jkg-1K-1)	3249
Specific heat of the equiaxed and columnar phase, c_e, c_c	1827
Latent heat of fusion at T_E, Δh (Jkg-1)	$3.138\cdot10^5$
Mass diffusivity of the liquid phase, D_l (m2s-1)	$4.8\cdot10^{-9}$
Mass diffusivity of the equiaxed and columnar phase, D_e, D_c	0
Partition coefficient, k (wt.%/wt.%)	0.003
Eutectic concentration, C_E (wt.%)	80.3
Eutectic temperature, T_E (K)	259.2
Liquidus temperature, T_L (K)	$629.403 - 4.61\cdot C_l$
Thermal expansion coefficient, β_T (K-1)	$3.23\cdot10^{-4}$
Solutal expansion coefficient, β_c (wt.%-1)	$3.65\cdot10^{-4}$
Gibbs-Thomson coefficient, Γ (mK)	$5\cdot10^{-8}$
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

The columnar dendritic growth is also responsible for the grain size formation at the two sidewalls and at the bottom of the mould. 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_0. On the other hand, the horizontal solid layer at the bottom grew homogeneously throughout the process. In recently published work, a direct comparison of the computed and measured images at the end of the solidification showed a qualitatively good agreement with experimental data for the distribution of the columnar and equiaxed dendritic structure in the bottom part of the mould [15], where no break-off interfered with the growth. To monitor the growth of the mushy zone, its thickness was therefore measured at the centre of the cell and perpendicular to the bottom cell wall. The results of the measurement of the thickness of the mushy zone d versus process time are shown as dots in Fig. 1, where different colours correspond to different experiments with the same initial concentration of NH_4Cl. The calculated thickness of the mushy zone is shown as blue line in Fig. 1. Initially, d is increased linearly with time, later it will be increased with the square root of time [7] as follows

$$d = \alpha\sqrt{(t - t_*)} - \beta\,, \tag{7}$$

where t is the solidification time, t_* the time after the linear growth period and β the thickness after the linear growth period. α was computed for each point in the linear and in the square root of t regime, as $\alpha_{lin} = \frac{d+\beta}{t-t_*}$ and $\alpha_{\sqrt{t}} = \frac{d+\beta}{\sqrt{(t-t_*)}}$, respectively. Fig. 2 shows plots of $\alpha_{\sqrt{t}}$ for the 3 different experiments shown in Fig. 1. The average values of the α factors show only small variations between the different regimes and are therefore considered suitable as a parameter to validate the numerical computations of the solidification process. The magnitude of the $\alpha_{\sqrt{t}}$ factor is related to the local thermal and solutal gradient at the solidification front [16]. The observed decrease of α can therefore be attributed to the fact that both gradients decrease with solidification time. Overall, the numerical simulation based on the proposed multiphase model has produced qualitatively similar grain distribution with respect to the experiment. The temperature dependence of the thermophysical parameters has to be considered to obtain a better agreement with experimental data.

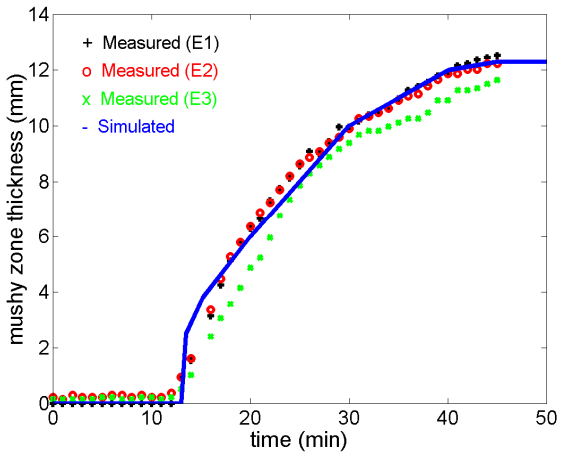

Figure 1: Measured thickness of the columnar/equiaxed zone in the centre of the bottom wall for three different experiments with the same initial concentration, 29.5 (wt.%) NH_4Cl, and cooling rate versus time

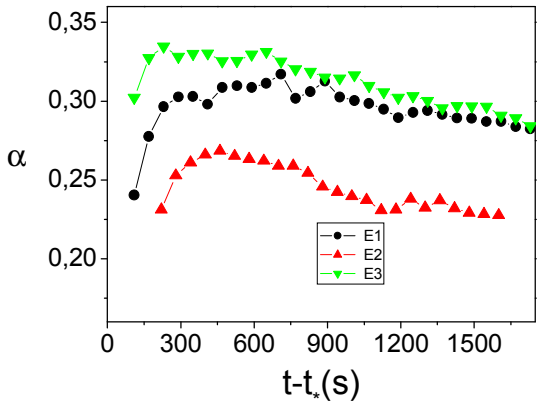

Figure 2: Evolution of α factor (definition is given in the text) during solidification of the 3 experiments presented in Fig. 1

Summary

This work represents benchmark experiments with NH_4Cl-H_2O solutions designed to test a proposed numerical solidification model dealing with combined columnar and equiaxed growth. The morphology of equiaxed grains is approximated by ideal spheres. The columnar dendrite trunks are assumed to be cylinders. For a quantitative comparison of the numerical model and the measured solidification process the thickness of the mushy zone was computed and measured at the centre of the cell and perpendicular to the bottom cell wall. The results show a good agreement for the growth of the mushy zone in the centre and bottom region of the measurement cell. For a better agreement in the top region of the cell the observed break-off of horizontally growing NH_4Cl caused by a interrelation of gravity and strong flows (driven by thermal and solutal buoyancy) along the walls has to be implemented in the numerical model.

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