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On measurement and prediction of the solid fraction within mushy layers

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We present a mathematical model of a mushy layer that incorporates transport of heat and solute by the flow of interstitial fluid caused by expansion during solidification. We also reinterpret the data of Shirtcliffe et al. J. Crystal Growth 113 (1992) 566, by taking into account the anisotropy of the mushy layer, in order to determine better estimates of the local solid fraction in mushy layers produced experimentally. Very good agreement is found between the theoretical predictions and the experimental results, which suggests that certain geometrical effects that were thought to have influenced the experimental measurements may in fact be negligible.

1. Introduction

In many important cases of natural and industrial solidification (particularly of multi-component melts), a mushy layer of dendritic crystals and interstitial melt forms between the growing solid region and the original melt. It has long been realized that flow of the melt due to solidification shrinkage (the change in specific volume that typically accompanies changes of phase) is an important mechanism causing macrosegregation in both metallurgical systems [1,2] and in geological systems such as magma chambers [3]. In addition, there have been quantitative estimates made of the extent of such macrosegregation using modifications of the Scheil equation coupled with estimates of the local temperature field during solidification [2,4]. In this paper, we describe a model that can be used to make direct predictions of the local solid fraction within a mushy layer, and hence can be used to calculate the extent of macrosegregation in a solidifying alloy.

It is also important to know the solid fraction in a mushy region for other reasons. The mushy layer forms a porous medium (matrix) through which the interstitial melt can flow in response to its own buoyancy in a gravitational field or to externally applied forces. The permeability of the mushy layer depends in large part upon the local liquid fraction, which in turn is determined by various internal physical processes involved in solidification. It is essential to know the permeability before any flow of the melt can be analyzed. To this end, there has recently been renewed interest in measuring the liquid fraction of mushy layers in laboratory experiments [5,6].

Chen and Chen [6] used X-ray tomography to measure the solid fraction (thence the liquid fraction) in a mushy layer after the completion of an experiment, while Shirtcliffe et al. [5] (herein referred to as SHW) developed a simple electrical method for making in situ measurements of the solid fraction in a mushy layer as it evolves during an experiment. SHW compared their findings with the predictions of a mathematical model [7] and found reasonable agreement for a range of experimental conditions. However, the theory gave consistently lower values of the solid fraction than SHW determined from their experimental data. The authors attributed this discrepancy to two effects: the neglect in the theory of the expansion upon change of phase from liquid to solid, and certain "geometrical effects" in the experiments such as the preferential growth of

solid along one of the electrodes of the measuring device. In this paper, we present results of a new theoretical model that incorporates the effects of expansion, and we reinterpret the data of SHW, by taking into account the anisotropy of the electrical conductivity of the mushy layer, to show that any geometrical effects are negligible.

In section 2, we describe briefly the experiments of SHW and the method they used to infer the solid fraction from their measurements of resistance. In section 3, we describe the orthotropic nature of the mushy layer, and develop a new expression relating the measured resistance to the local solid fraction. The theoretical model is outlined in section 4, and its predictions of solid fraction are compared with the experimental results in section 5, where conclusions are drawn regarding the validity of the theoretical model and the accuracy of the experimental technique for measuring solid fractions in general mushy layers.

2. The experimental method

The experimental arrangement employed by SHW is shown in fig. 1. Details of the apparatus are given in their paper. Briefly, an aqueous solution of sodium nitrate was cooled from below in a rectangular container to produce a mushy layer of ice crystals with solution enriched in sodium nitrate between them.

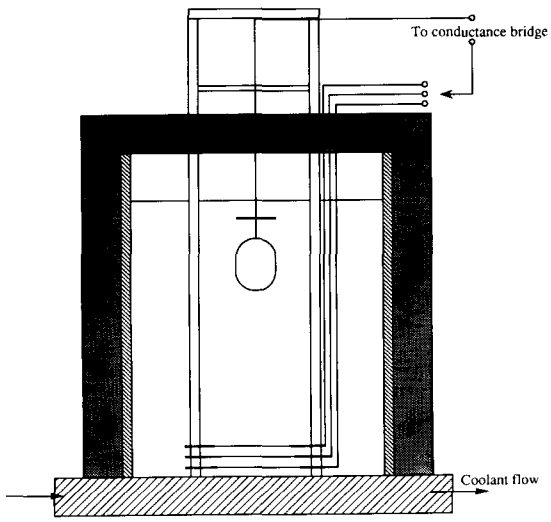

Fig. 1. A schematic diagram of the experimental apparatus used by Shirtcliffe et al. [5].

There were three thin wires stretched horizontally at heights z_i above the cooled boundary. Each of these wires formed one electrode of a conductivity cell, the other electrode in each case being a carbon block of relatively large surface area suspended in the solution high above the cooled boundary. As the mushy layer grew past each wire, the ice dendrites covered parts of the wire, decreasing the length of the wire in contact with the fluid, and thereby increasing the resistance of the medium, since the solid has negligible conductance compared with the liquid.

The experiments performed by SHW consisted of measuring the resistance of the conductivity cell. Two assumptions were then made: that the resistance of the cell was governed principally by the resistance of the medium in the vicinity of the thin wire forming the lower electrode of the cell; and that a proportion ϕ (equal to the local solid fraction of the mushy layer) of the wire was covered in ice, through which no current flowed. The solid fraction ϕ was therefore determined from the expression

$$1 - \phi = K/\gamma R, \tag{2.1}$$

where R is the measured resistance of the conductivity cell, and γ is the electrical conductivity of the interstitial fluid near the wire. The cell constant K was determined from $K = \gamma_0 R_0$, where R_0 and γ_0 are, respectively, the resistance of the cell and conductivity of the solution at the start of an experiment, before ice had begun to grow. The local electrical conductivity of the interstitial fluid γ depends upon the temperature and concentration of the fluid, which variation can be adequately approximated by

$$\gamma = \gamma_l[1 - 0.015(20 - T)], \tag{2.2}$$

where T is the temperature of the liquid in degrees Celcius, and γ_l is given by

$$\gamma_l(C) = (0.9809C - 1.79 \times 10^{-2}C^2 + 1.13 \times 10^{-4}C^3)\ \Omega^{-1}\ \mathrm{m}^{-1}. \tag{2.3}$$

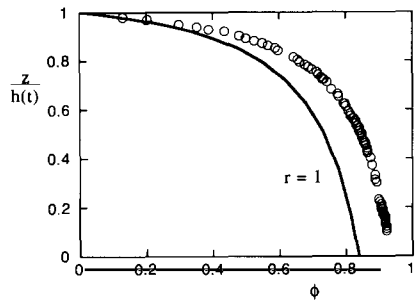

Fig. 2. Comparison of the measurements of solid fraction determined using eq. (2.1) with the predictions of a theoretical model that neglects any convection of interstitial fluid caused by expansion during solidification. The initial concentration of the solution was 5.5 wt% $NaNO_3$. The other parameter values are given in table 1. The experimental data are from ref. [5].

Fig. 2 shows a plot of the measured values of ϕ, according to eq. (2.1), compared with the theory of Worster [7] for an initial concentration $C_0 = 5.6$ wt% $NaNO_3$. This plot did not appear in SHW, since these authors further adjusted their data to account for possible geometrical effects in the experiments. We see that the theory predicts values of ϕ that are about 10% less than those determined experimentally. We believe that this discrepancy is due partly to simplifying assumptions in the theory and partly to the eq. (2.1) used to infer the solid fraction from the measurements of resistance.

Table 1
The parameter values used in the calculations leading to fig. 5

Parameter	Value	Units
m	0.4	°C
L	73.6	cal cm^{-3}
k_s	5.3×10^{-3}	cal g^{-1} s^{-1} $°C^{-1}$
k_l	1.3×10^{-3}	cal g^{-1} s^{-1} $°C^{-1}$
ρ_s	0.92	g cm^{-3}
ρ_l	1.25	g cm^{-3}
c_s	0.44	cal cm^{-3} $°C^{-1}$
c_l	1.0	cal cm^{-3} $°C^{-1}$
T_∞	20	°C
T_B	−14.0	°C

3. The orthotropic conductivity of the mushy layer

The mushy layer usually takes the form of a forest of solid, dendritic or sheet-like crystals, oriented principally along the direction of strongest thermal gradient, with fluid filling the interstices. The ice dendrites in the experiments of SHW are therefore growing preferentially perpendicular to the axis of the wire that forms the lower electrode of the conductivity cell. Given this geometrical arrangement of the insulating ice crystals, the conductivity of the mushy layer can be thought of as being locally orthotropic, with a conductivity tensor given by

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma_v & 0 & 0 \\ 0 & \gamma_h & 0 \\ 0 & 0 & \gamma_h \end{pmatrix}, \tag{3.1}$$

where γ_v is the effective conductivity in the vertical direction (parallel to the primary arms of the dendrites) and γ_h is the effective conductivity of the medium in the horizontal plane. We can estimate the effect of anisotropic conductivity upon the current through the cell by considering the current from a thin horizontal wire in a semi-infinite domain. Such a calculation shows that the resistance R of the cell and the conductivity of the medium are related approximately by

$$1/R \propto (\gamma_h \gamma_v)^{1/2}. \tag{3.2}$$

It remains to estimate γ_v and γ_h in the mushy layer in terms of the local solid fraction ϕ. Since the solid phase takes the approximate form of rods or sheets aligned vertically, the conductivity along the direction of preferential growth can be estimated by

$$\gamma_v \approx \gamma(1-\phi), \tag{3.3}$$

where γ is the local conductivity of the interstitial fluid. If expression (3.3) were also used to determine γ_h, then expression (2.1) used by SHW would be recovered. In fact, eq. (3.3) gives an upper bound for the conductivity of a general medium, and this bound is attained for the special case of parallel rods or lamallae when the heat flux vector is in the same parallel direction

[8]. Lower upper bounds for statistically isotropic two- and three-dimensional media have been derived by Hashin and Shtrikman [9] (ref. [8], p. 198). Therefore, on the assumption that the mushy layer is statistically isotropic in horizontal planes, we use the Hashin–Shtrikman upper bound for two-dimensional media to estimate

$$\gamma_h \approx \gamma \frac{1-\phi}{1+\phi}, \tag{3.4}$$

assuming that the ice crystals are perfectly insulating. The Hashin–Shtrikman lower bound is zero in this case. This is a tight bound, since it is achieved by a medium composed of composite spheres (ref. [8], p. 198) We note also that eq. (3.4) gives the correct asymptotes for a dilute array of circles ($\phi \ll 1$) [10] and for a concentrated rectangular array of squares ($1-\phi \ll 1$). By combining expressions (3.2)–(3.4), we find that

$$\frac{1-\phi}{\sqrt{1+\phi}} = \frac{K}{\gamma R} \equiv A, \tag{3.5}$$

which can be solved for ϕ to give

$$\phi = \tfrac{1}{2}\left(2 + A^2 - \sqrt{A^4 + 8A^2}\right). \tag{3.6}$$

Expression (3.6) will be used later (in fig. 5) in place of (2.1) to estimate the solid fraction from the measured resistances.

4. A theoretical model of the mushy layer

When a melt solidifies, the solid usually has a different density than the melt. The difference in specific volume induces a flow of the melt towards the solid if the solid has a greater density than the melt, or away from the solid otherwise. This flow alters the rate of transport of heat and mass, thereby affecting the rate of solidification and the macrosegregation of a binary system. These effects are particularly important when the liquid fraction of the medium is small.

Quantitative estimates of the macrosegregation caused by shrinkage have previously been made by Flemings and Nereo [2] and by Mehrabian et al. [4] using measured values of the evolving temperature field. More accurate calculations can be made by solving the full set of coupled transport equations for mass, heat and solute.

In this section, we extend the mathematical model of a mushy layer developed by Worster [7] by incorporating effects due to the expansion of the melt phase as it solidifies. We take the segregation coefficient to be zero, which is a good approximation for aqueous salt solutions. Many additional features of this model will be discussed in a future publication.

The governing equations for the mushy layer are given by the local conservation equations for heat and solute, which can be expressed in the following differential form:

$$c_m \frac{\partial T}{\partial t} + c_l \boldsymbol{U} \cdot \nabla T = \nabla \cdot (k_m \nabla T) + \mathscr{L}_s \frac{\partial \phi}{\partial t}, \tag{4.1}$$

$$(1-\phi)\frac{\partial C}{\partial t} + \boldsymbol{U} \cdot \nabla C = rC \frac{\partial \phi}{\partial t}. \tag{4.2}$$

The temperature T and the composition of the interstitial liquid C are assumed to be uniform over length scales typical of the interdendritic spacing. The volume fraction of solid dendrites is denoted by ϕ, while $\boldsymbol{U}$ represents the volume flux of interdendritic fluid. The physical parameters in these equations are the specific heat per unit volume c, the latent heat per unit volume of solid $\mathscr{L}_s$, the thermal diffusivity k, and the density ratio $r = \rho_s/\rho_l$, where the subscripts "s", "l" and "m" denote properties of the solid, liquid, and mushy phases, respectively. The thermal properties of the mush are taken to be volume-fraction-weighted averages of the properties of the individual phases, so that

$$c_m = \phi c_s + (1-\phi)c_l, \tag{4.3}$$

$$k_m = \phi k_s + (1-\phi)k_l, \tag{4.4}$$

and the diffusion of solute is neglected. Expression (4.4) is only approximate, since transport properties depend on the internal morphology of the two-phase medium [8], but it has been found to lead to good agreement with experimental results, as shown by Worster [7] and Kerr et al. [11].

Unlike the model of Worster [7], eqs. (4.1) and (4.2) include the transport of heat and solute by convection as well as by diffusion. The velocity field $\boldsymbol{U}$ is determined by mass conservation, represented by the continuity equation

$$\nabla \cdot \boldsymbol{U} = (1 - r)\, \partial\phi/\partial t. \tag{4.5}$$

Notice that the divergence of the velocity field is not zero, rather it depends on the rate of change of the solid fraction in a way determined by the density ratio r. The terms $\mathscr{L}_s\, \partial\phi/\partial t$ and $rC\, \partial\phi/\partial t$ on the right-hand sides of the above conservation equations, respectively, express the release of latent heat into the mush and of solute into the interstitial fluid. The rate of change of the solid fraction couples eqs. (4.1), (4.2) and (4.5), and is obtained implicitly through the equilibrium condition

$$T = T_l(C) = -mC, \tag{4.6}$$

which says that the temperature everywhere is equal to the local liquidus, where m is the slope of the liquidus curve.

The equations above constitute a full set of governing equations for the mushy layer. Three interfacial conditions that express conservation of heat, solute and mass at the mush–liquid interface can be derived from eqs. (4.1), (4.2) and (4.5). These can be expressed as

$$\phi = 0, \tag{4.7a}$$

$$[\boldsymbol{n} \cdot \boldsymbol{U}] = 0, \tag{4.7b}$$

$$[\boldsymbol{n} \cdot \nabla T] = 0, \tag{4.7c}$$

where $\boldsymbol{n}$ is a unit vector normal to the interface and $[\cdots]$ denotes the jump in the enclosed quantity across the interface. The interfacial conditions (4.7) are appropriate once the condition of marginal equilibrium [7] is taken into account, and the the limit of zero solutal diffusivity is applied [11].

5. Results and discussion

As in previous studies [7], the system of partial differential equations described in section 4 admits a similarity solution for solidification from a cooled, planar boundary, as illustrated in fig. 3, in which the mush–liquid interface has position

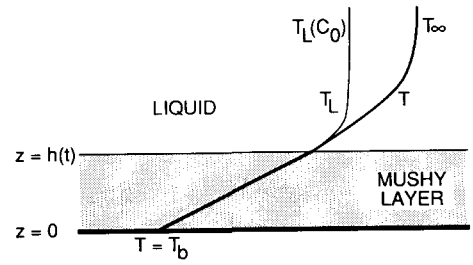

Fig. 3. A mushy layer grows in the positive z-direction and has depth $h(t)$ after a time t has elapsed. The boundary $z = 0$ is maintained at the fixed temperature T_b, while the melt far from the interface has temperature T_∞ and concentration C_0.

$$h(t) = 2\lambda\sqrt{\kappa_l t}\,, \tag{5.1}$$

where $\kappa = k/c$ is the thermal diffusivity and λ is a constant to be determined as part of the solution. The dependent variables are then functions only of the similarity variable

$$\xi = z/2\sqrt{\kappa_l t}\,. \tag{5.2}$$

Thus, for example, the solid fraction $\phi(\zeta)$ is a function of the single variable

$$\zeta = z/h(t) = \xi/\lambda. \tag{5.3}$$

The system of equations presented in section 4 was solved numerically in similarity form and the

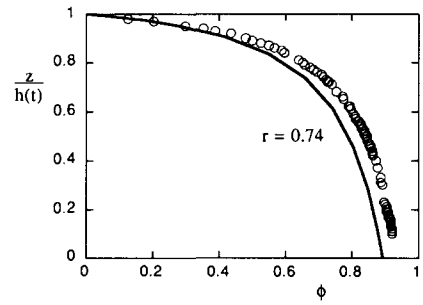

Fig. 4. Comparison of the measurements of solid fraction determined using eq. (2.1) with the predictions of a theoretical model that incorporates convection of interstitial fluid caused by expansion during solidification. The initial concentration of the solution was 5.6 wt% $NaNO_3$. The other parameter values are given in table 1. The experimental data are from ref. [5].

results for one set of parameters is displayed in fig. 4 along with the experimental values that were interpreted using (2.1) to calculate the solid fraction. Notice that the agreement between the theoretical and experimental results is better than when expansion was ignored in the theory (fig. 2) but the discrepancy is still about 5%. When, however, expression (3.6), rather than (2.1), is used to calculate the solid fraction from the measured resistances, one obtains the results displayed in figs. 5a–5d. In these figures, the theoretical calculations for ϕ as function of ζ are compared with the experimental data interpreted in the way described in section 3. As can be seen, there is now very good agreement between the experimental data and the theoretical predictions.

The experimental method, pioneered by SHW and extended herein, and the theoretical model detailed in section 4 are both new techniques for determining the solid fraction in mushy layers. The theoretical model is based upon many approximations, and the experimental method requires that a number of assumptions be made in order for the solid fraction to be deduced from the measurements of resistance. That the results of the two approaches agree so well is very encouraging but should not yet be taken as conclusive evidence of the validity of either the theory or the experimental technique. However, the good agreement shown in fig. 5 is suggestive that the geometrical effects proposed by SHW to explain some of the discrepancy they found between theory and experiment may be negligible.

One of the assumptions on which the experimental technique is based is that the resistance of the conductivity cell depends dominantly on the electrical conductivity of the neighborhood of the thin wire that forms the lower electrode. Another implicit assumption is that the shape of the current paths are not influenced by the presence of the mushy layer. Neither of these assumptions are strictly valid. The electric field around a long cylindrical wire only decays inversely with dis-

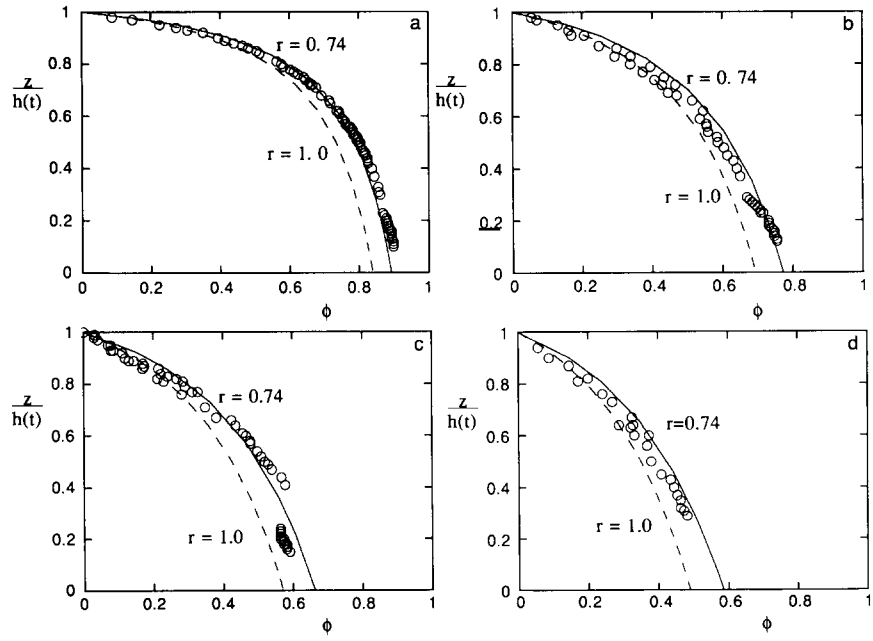

Fig. 5. Comparison of the measurements of solid fraction with the predictions of a theoretical model that takes into account the convection of interstitial fluid caused by expansion during solidification. The initial concentration of the solution is: (a) 5.6 wt% $NaNO_3$, (b) 10.75 wt% $NaNO_3$, (c) 15.0 wt% $NaNO_3$ and (d) 17.8 wt% $NaNO_3$. The other parameter values are given in table 1. The original experimental data were supplied by T.G.L. Shirtcliffe and interpreted according to eq. (3.6).

tance from the center of the wire, which means that the resistance between the wire and a concentric outer cylinder (for example) increases logarithmically with the distance between the wire and the cylinder. Thus the instrument is measuring some integrated property of the mushy layer and not simply the local properties of the layer near the wire. The second assumption should also be questioned, since the current paths must pass through a medium of variable conductivity and will therefore be refracted by the medium.

These concerns point to the need to devise more controlled experiments, and perhaps to improve the measurement technique before the experimental results can be used conclusively to confirm the accuracy of the theoretical predictions. A modified set up for the experiment described in section 2 has been proposed and used by Shirtcliffe and Kerr [12] in which the two electrodes measuring the resistance of the cell are two wires stretched horizontally across the tank at the same height. These wires are separated by 5 mm horizontally, and have a diameter of 0.20 mm. The electric field around the two wires has dipole character and decays inversely with the square of the distance from the center of the dipole. This set up should in principle, therefore, provide a more local measurement of the conductivity of the mushy layer and allow better measurements of the solid fraction ϕ to be made.

The parameters for the two wire experiment as well as values of ϕ interpreted from the resistance measurements using expression (2.1) were made available to us by Shirtcliffe and Kerr. The parameters for the experiment were used to generate a theoretical plot of the change in solid fraction throughout the depth of the mushy layer. The experimental values of ϕ were recalculated using expression (3.6) and compared to the theoretical values. The agreement between the theoretical and the experimental results was found to be no better than 10%. While it is possible that ice grew preferentially on the electrodes causing the resistance measurements to be too high, as suggested by Shirtcliffe and Kerr, some explanation is required for why such effects are apparently negligible in the single-wire method. Another possible source of error is that the spacing between the wires in the two-wire experiment should be large compared to the typical spacing between the solid particles in order that the mushy layer can be treated effectively as a random medium. The typical spacing between dendrites is about 1 mm, so a spacing of 5 mm between the two wires might not have been large enough. There is clearly a need for further investigations in order to establish the accuracy of the various experimental techniques that have been proposed.

6. Conclusions

In this paper, we have extended a theoretical model of mushy layers [7] to include the effects of expansion upon change of phase, and we have reinterpreted the data from previous experiments by taking into account the anisotropy of the electrical conductivity of the mushy layer. As a result, we have obtained much better agreement between theory and experiment than has previously been reported [5].

The purpose of this continuing work is twofold: to develop an accurate instrument for the measurement of solid fractions in mushy layers that can be used in many different experimental situations, particularly those in which convection of the interstitial fluid is important; and to confirm the predictions of mathematical models of the solidification of alloys than can then be used with confidence to determine the behavior of experimentally inaccessible systems.

The convection due to expansion during change of phase, which has been incorporated in the theoretical model described in section 4, is an important process affecting global transport of solute within the system. Such transport can cause significant macrosegregation in castings [2] and in geological systems such as magma chambers [3]. Although in terrestrial environments, buoyancy-driven convection is usually a more significant cause of macrosegregation, in a micro-gravitational environment, convection due to expansion may be the dominant process leading to macrosegregation within cast alloys.

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