SOLIDIFICATION AND COMPOSITIONAL CONVECTION OF A TERNARY ALLOY

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Summary We describe an experimental study where an aqueous solution of potassium nitrate and sodium nitrate is cooled from below resulting in the formation of two mushy layers. A density reversal is observed that leads to a transition from a convective regime to a diffusive regime and significantly alters the structure and growth rate of the mushes.

INTRODUCTION

The formation of solids from a liquid melt often generates fluid flows due to convection, which can effectively transfer heat and mass and significantly influence the structure and growth rate of the solid phase. Preferential incorporation of some components into the solid and rejection of others gives rise to one or more mushy layers between the melt and composite solid. Solidification of a ternary alloy reveals dynamics not observed in well-studied binary alloys. One such process is a density reversal, which we consider here.

Aitta, Huppert and Worster [1] initiated an experimental study of ternary alloys by cooling from below a simple alloy of two salts dissolved in water. In these experiments the initial concentrations of the alloy were chosen so that the compositional fields were stably stratified at all times. Convection was absent and the growth of the mushy layers and composite solid were diffusion-limited. In our experiments we considered initial conditions such that there was a transient period during which convection influenced the growth rate of the mushes.

METHODS

The alloy selected consisted of two salts, potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$) dissolved in water. This system was chosen principally because it conforms to a simple phase diagram with liquidus temperatures easily reached with typical lab equipment. Concentration measurements of KNO_3 and $NaNO_3$ in water were made using a Varian SpectrAA flame atomic absorption spectrometer. Experiments were conducted in a rectangular Perspex tank with internal dimension 20 cm by 20 cm, which was filled with solution to a depth of 35 cm. The walls and roof were insulated while the brass base allowed coolant to flow through it and cool the plate evenly.

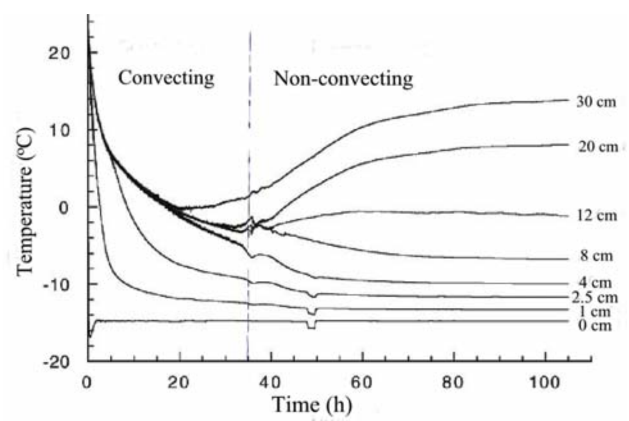
Initial concentrations were chosen so that KNO_3 solidified in the upper, primary, mush and KNO_3 and H_2O solidified in the lower, cotectic mush. The baseplate could be maintained at a constant temperature below the cotectic temperature, but above the eutectic temperature so that in the experiments discussed here no composite solid formed. Temperature measurements were made at various heights near the center of the tank using glass bead thermistors, including one embedded in the baseplate. Convection was monitored using a shadowgraph technique and the heights of the two mushy layers were determined by visual observations.

OBSERVATIONS AND MEASUREMENTS

Crystal formation began approximately one minute after coolant entered the baseplate, and the plate was completely covered with crystals after two minutes. Strong convection that kept the entire tank well mixed developed within the first five minutes of each experiment. The crystals initially had a thick fiber-like structure that evolved into a thinner shape after one or two hours. The mushes remained flush against the side of the tank while the system was convecting, and no chimneys were observed.

After a few hours the cotectic mush grew faster than the primary mush, thus reducing the depth of the upper mush layer. As the primary mush became thin, convection weakened and no longer kept the entire depth of the tank well mixed. Eventually the cotectic mush overtook the primary mush and convection ceased completely. This transition took 1 to 2 hours compared with a total convection time of 25 to 35 hours. As the single mush that remained continued to grow, a visible interface identifiable by a change in crystal structure or solid fraction remained visible at the height where the cotectic mush overtook the primary mush. Above this interface a gap developed between the mush and the side of the tank that was probably due to external heating from the lab.

Figure 1 shows the temperature traces at various heights above the baseplate in an experiment where the baseplate was maintained at a temperature of -14.75 ± 0.05 °C. Convection kept the liquid well mixed and the temperature uniform in the melt. As thermistors entered the mush the traces fell away from the uniform temperature. Convection stopped completely after 35 hours and as diffusion started to govern the dynamics, the melt became thermally stratified. The sharp drop in temperature seen around 48 hours was due to accidental error in the control setting. Figure 2 shows the heights of the primary and cotectic mushes from the same experiment as in figure 1. This plot shows the cotectic mush overtaking the primary mush and altering the growth rate of the remaining mush layer. Concentration measurements (not shown here) of samples removed from the melt during convection fall on the tie line between the liquidus point and the cotectic curve with concentrations moving towards the cotectic curve with increasing time. Concentration measurements of samples removed from within the cotectic mush after convection stopped collapsed on the cotectic curve with concentrations moving towards the eutectic point with increasing depth in the mush.



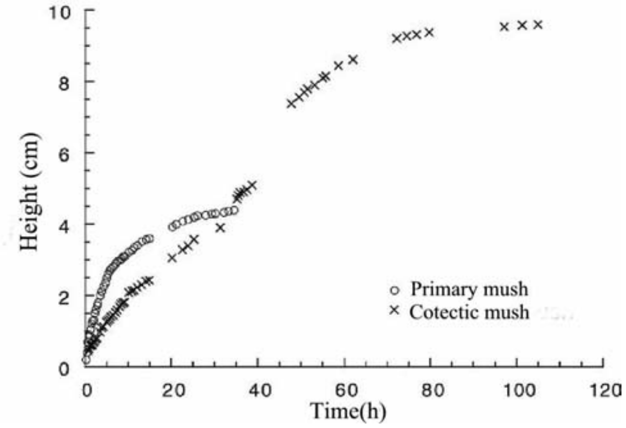


Figure 1 (*left*). Temperature traces of the residual liquid from various heights above the baseplate. The dashed vertical line marks the end of convection at approximately 35 hours. The drop in temperature at 48 hours is due to personal error.

Figure 2 (*right*). The height of the primary and cotectic mushes from the same experiment as in figure 1. Convection stopped at approximately 35 hours when the cotectic mush overtook the primary mush.

GLOBAL CONSERVATION MODEL

To describe our experiments we adopt a one-dimensional, global conservation model that is an extension of the binary model [2] including convection [3]. As opposed to the diffusion-limited model, the inclusion of convection implies that the solid fractions in the two mush layers are time-dependent. The model begins with equations for the conservation of heat and exact integral equations for conservation of solute in each layer. Then a shape assumption is applied to the solid fractions to simplify the system. Here we assume that the solid fractions are depth-averaged values so that they are independent of height. We further assume that local thermodynamic equilibrium holds throughout the mushy layers so that temperature and solute concentrations conform to the linear liquidus relationships. This assumption further allows us to neglect solutal diffusion in the mushes. Boundary conditions are provided at the interfaces by using the ternary phase diagram, and the growth rates are coupled by conservation of heat at the interfaces.

The model is initiated with empirical values for the solute and heat fluxes, which are determined by the time rate of change of concentration and temperature in the melt. The Stefan condition is introduced at the interfaces, which describes a balance between the latent heat release upon solidification, heat conduction through the solid and, in the case of the upper mush layer, a convective heat flux. The model was found to give good results for the interface positions of the two mushy layers up until the point where the cotectic mush overtakes the primary mush. Further work is required to accurately model the dynamics of the transition from a convective to a diffusive regime. The reader is referred to Thompson *et al.* [4] for the full derivation of the global conservation model.

CONCLUSIONS

We have shown experimentally that a density reversal can lead to the reduction of the number of distinct mushy layers in a solidifying alloy. This transition can have profound effects on the structure and growth rate of the solidifying components, and plays an important role in dynamics of more complex multi-component alloys.

References

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