FRECKLES IN DIRECTIONAL SOLIDIFICATION OF BINARY ALLOYS

Sergio D. Felicelli
División Mecánica Computacional
Centro Atómico Bariloche, 8400 Bariloche, Río Negro, Argentina

Juan C. Heinrich
Department of Aerospace and Mechanical Engineering
University of Arizona, Tucson, Arizona 85712, U.S.A.

David R. Poirier
Department of Materials Science and Engineering
University of Arizona, Tucson, Arizona 85712, U.S.A.

RESUMEN

Se presenta un modelo matemático de solidificación, que simula la formación de inhomogeneidades en la concentración de soluto cuando una aleación binaria es solidificada direccionalmente. El crecimiento de la zona bifásica o dendrítica se calcula resolviendo las ecuaciones acopladas de transporte de momento, energía y soluto, más las relaciones de equilibrio termodinámico impuestas por el diagrama de fase de la aleación. Cálculos realizados en aleaciones plomo-estaño muestran que la convección termosalina que se desarrolla en la zona dendrítica durante la solidificación puede ocacionar inhomogeneidades fuertemente localizadas en la composición final de la aleación.

ABSTRACT

A mathematical model of solidification is presented. The model simulates the formation of segregation defects known as "freckles" during directional solidification of binary alloys. The growth of the two-phase or dendritic zone is calculated solving the coupled equations of momentum, energy and solute transport, as well as mantaining the thermodynamic constraints dictated by the phase diagram of the alloy. Calculations in lead-tin alloys show that the thermosolutal convection in the dendritic zone during solidification can produce heavily localized inhomogeneities in the final alloy composition.

INTRODUCTION

Freckles are segregation defects, at the macroscopic scale, that are found in many unidirectionally solidified alloys. During directional solidification, a liquid alloy is cooled from below, and solidification is effected upwards into the melt. Today's directional solidification processes can produce high perfomance materials, suitable for components that must operate under severe conditions of temperatures and stresses, as in the case of gas turbine blades of aero engines. A columnar microstructure, with all the grain boundaries running in the longitudinal direction of the casting, prevents the usual failures associated with grain boundaries that are transverse to the applied stress.[1]

Improper control of species transport, however, occurring by advection and diffusion

during solidification, can result in localized regions of segregation with unacceptable levels of inhomogeneity. Freckling is one of the most severe types of segregation. This nonuniformity of composition reflects itself in an undesirable variation in mechanical, chemical, electrical, magnetic or other physical properties of the alloy and thus leads to an inferior perfomance during service. In ingot production, an excessive number of defects can require a large amount of cropping, at a considerable cost of energy and material.

The analysis of the transport mechanisms relevant to multiconstituent phase change encompasses a broad spectrum of engineering and scientific disciplines such as process metallurgy, thermodynamics, heat and mass transfer and fluid mechanics. A comprehensive approach that integrates these areas in a consistent framework is essential to predict realistic system behaviour.

When a molten alloy, initially at uniform composition, is solidified, several physical factors contribute to a final solid of nonuniform composition. First, the density of the solid and liquid phases (ρ_S and ρ_L, respectively) are different, resulting either in liquid flow towards the freezing regions to feed shrinkage if $\rho_S > \rho_L$, or flow away from the solid liquid interface if $\rho_S < \rho_L$. Second, temperature and solute gradients develop at the solid-liquid interface because of the latent heat of fusion released during solidification. Third, in most systems the alloying elements have different solubilities in the solid and liquid phases; hence the phases can become preferentially enriched or depleted of alloying elements. There is little that can be done to alter these three factors, which are dictated solely by fundamental physical and chemical laws governing the atomic or molecular arrangements in the solid and liquid states. The final solid formed is thus necessarily inhomogeneous in composition [2].

It is now widely accepted, however, that none of these factors leads to severe segregation defects like freckles, but they are a direct consequence of a fourth factor: the gravity driven fluid flow [Refs. 3-6]. In multicomponent alloys, the density of the liquid varies with both temperature and concentration. Hence, natural convection can be induced by both temperature and concentration gradients present during solidification. Also, unlike pure substances, the freezing of alloys takes place over a range of temperatures at which the solid and liquid phases coexist in equilibrium, depending on the local composition. Temperature and concentration gradients at the solid/liquid interface are such that morphological instabilities cause the interface to deviate from the planar form observed in the solidification of pure substances. Rather the solid propagates in the form of tree-like protrusions called "dendrites", forming a mixture of the dendritic solid and interdendritic liquid known as the "mushy zone", whose physical substructure is microscopic and has a length scale on the order of 100μm. The segregation produced by the three factors mentioned in the previous paragraph is generally restricted to these length scales, and is known as microsegregation. The advection of segregated solid and liquid phases that accompanies solidification leads to a macroscopic redistribution of constituents known as macrosegregation; freckles or channels is a typical manifestation.

In early papers on modeling directional solidification of dendritic alloys [e.g., Refs. 7-8], thermosolutal convection in the liquid was neglected and these models could not account for the formation of freckles. More recently, Bennon and Incropera [9] and Beckermann and Viskanta [10] modeled horizontal solidification of alloys, taking into account thermosolutal convection. Their calculations showed strong double-diffusive effects and the development of irregularities in the growth front, including pockets of segregated liquid within the mushy zone. None of these studies, however, simulated freckle formation during vertical solidification.

Our investigations into the simulation of freckle formation began with the assumption that the volume fraction of liquid in the dendritic region does not change with time and is consistent with the non-convecting state of the system; the results were presented in

Heinrich et al. [11] and Nandapurkar et al. [12]. This assumption, although valid at the onset of convection does not hold after convection starts, and was then relaxed to allow the dendritic region to develop according to the local conditions of equilibrium. The resulting numerical model, presented in Heinrich et al. [13] and Felicelli et al. [14], is the first to reproduce features of channel formation described in experimental work [3,4].

MATHEMATICAL MODEL

The model that has been implemented is two dimensional and can be readily extended to a 3D version. The physical situation consists of an initially liquid binary alloy contained in a rectangular mold which is cooled at the base at a specified rate. The alloy begins to solidify forming a dendritic zone comprising solid and liquid that advances upward, and the solidification proceeds until all the initial melt is completely solidified.

The dendritic zone (deemed the mushy zone by metal casters) is represented mathematically by an anisotropic porous medium of variable porosity, and it is free to develop according to thermodynamic constraints, i.e. it has no predetermined shape or size. The equations of conservation of mass, momentum, energy and solute content are solved in a two dimensional domain (Fig. 1) under the following assumptions:

(i) The flow is laminar.
(ii) Only solid and liquid phases are present, i.e. no pores form.
(iii) The solid and liquid phases have equal densities.
(iv) The density is constant except in the buoyancy term of the momentum equation (Boussinesq approximation).
(v) There is negligible diffusion of solute within the solid.
(vi) The solid does not convect.
(vii) The thermal properties are constant and equal in both the liquid and solid phases.

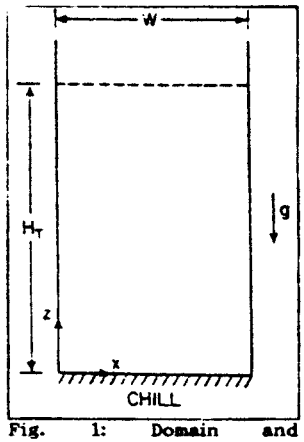

Fig. 1: Domain and coordinate system for vertical solidification

Based on these assumptions, the set of equations governing the conservation of mass, momentum, energy and solute content, can be written as [14,15]:

(continuity)

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0 \qquad (1)$$

(x-momentum)

$$\phi \frac{\partial (u/\phi)}{\partial t} + u \frac{\partial (u/\phi)}{\partial x} + w \frac{\partial (u/\phi)}{\partial z} = -\frac{\phi}{\rho_0} \frac{\partial p}{\partial x} + \nu_0 \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2} \right) - \frac{\nu_0 \phi}{K_x} u \qquad (2)$$

(z-momentum)

$$\phi \frac{\partial (w/\phi)}{\partial t} + u \frac{\partial (w/\phi)}{\partial x} + w \frac{\partial (w/\phi)}{\partial z} = -\frac{\phi}{\rho_0} \frac{\partial p}{\partial z} + \nu_0 \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial z^2} \right) - \frac{\nu_0 \phi}{K_z} w - \phi \frac{\rho}{\rho_0} g \tag{3}$$

(density)

$$\rho = \rho_0 [1 - \beta_T (T - T_0) - \beta_C (C_l - C_0)] \tag{4}$$

(energy)

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + w \frac{\partial T}{\partial z} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial z^2} \right) - \frac{L}{\bar{c}} \frac{\partial \phi}{\partial t} \tag{5}$$

(solute-content)

$$C_l = \begin{cases} C_L(T) \text{ (liquidus line in the phase diagram)} & \text{if } \phi < 1 \\ \bar{C} & \text{if } \phi = 1 \end{cases} \tag{6}$$

$$\bar{C}_s = \frac{1}{1 - \phi} \int_{\phi}^{1} k C_l \, d\phi \tag{7}$$

$$\frac{\partial \bar{C}}{\partial t} + u \frac{\partial C_l}{\partial x} + w \frac{\partial C_l}{\partial z} = D \left[\frac{\partial}{\partial x} \left(\phi \frac{\partial C_l}{\partial x} \right) + \frac{\partial}{\partial z} \left(\phi \frac{\partial C_l}{\partial z} \right) \right] \tag{8}$$

$$\phi = \frac{\bar{C} - \bar{C}_s}{C_l - \bar{C}_s} \tag{9}$$

where u and w are the components of the superficial velocity in the x and z directions. The x direction is horizontal, and the z direction is antiparallel to gravity. The superficial velocities are defined as

$$u = \phi \, u_l$$
$$w = \phi \, w_l$$

where u_l and w_l are the components of the interdendritic fluid velocity and ϕ is the volume fraction of interdendritic liquid. In the momentum equations, t is time, p is pressure, ν_0 is the kinematic viscosity and ρ_0 is the density at a reference state, g is the gravitational acceleration, and K_x and K_z are the permeabilities in the x and z directions, respectively. Equations used for permeabilities are given in [14], with $K_x = K_x(\phi, d_1)$ and $K_z = K_z(\phi, d_1)$, where d_1 is the primary dendrite arm spacing. The density, ρ, is assumed to be a linear function of the temperature, T, and the solute concentration of the liquid, C_l, where β_T is the thermal expansion coefficient, and β_C is

the solutal expansion coefficient. For the reference state, the concentration is that of the initial melt (C_0) and the temperature is the liquidus temperature (T_0) corresponding to C_0 on the equilibrium phase diagram. In Eq. (5), a is the thermal diffusivity, $\hat{c}$ is the heat capacity and L is the latent heat of fusion. Finally, in Eqs. (6-9), D is the solutal diffusivity in the liquid (assumed to be uniform), $\overline{C}$ is the local average composition of liquid and solid together, $\overline{C}_s$ is the average local composition of the solid, and k is the equilibrium partition ratio. In the mushy zone, the composition of the interdendritic liquid is given by the liquidus line in the phase diagram of the alloy, i.e. $C_l = C_L(T)$.

The differential equations were discretized using a finite element method based on rectangular bilinear Lagrangian elements. The numerical model uses a Petrov-Galerkin formulation for the convection dominated transport and a penalty function approximation to impose incompressibility. The system of the first order differential equations resulting from the semidiscrete Petrov-Galerkin approximation is integrated using a generalized Newmark method. The major features of the algorithm have been basically described in Heinrich [16] and Heinrich and Yu [17]. The detailed aspects of the method pertaining to a solidification process can be found in Heinrich [18], Heinrich and Felicelli [19], and Felicelli [15].

NUMERICAL SIMULATIONS

Numerical calculations have been performed that clearly display the formation of channels when a Pb-Sn alloy is solidified directionally. Here results for solidification of a Pb-10 wt pct Sn alloy are presented. As it is observed in DS castings, freckles are very narrow, with diameters usually smaller than 1 mm. This length scale is predictable and is on the order of the solute decay length scale, D/V, where D is the diffusivity of the solute in the liquid and V is the the solidification rate. An adequate mesh resolution, comparable to this length scale, must be used in order to reproduce the formation of freckles. Indeed, if the grid elements are too large, the simulation does not properly resolve the convection cells that lead to channel formation. This fact imposes a limitation on the size of the computational domain, because the location of channels and pockets of segregated liquid are unpredictable *a priori*; hence a mesh of uniformly sized elements must be used. A uniform mesh of 20 by 30 elements was used for the results reported here.

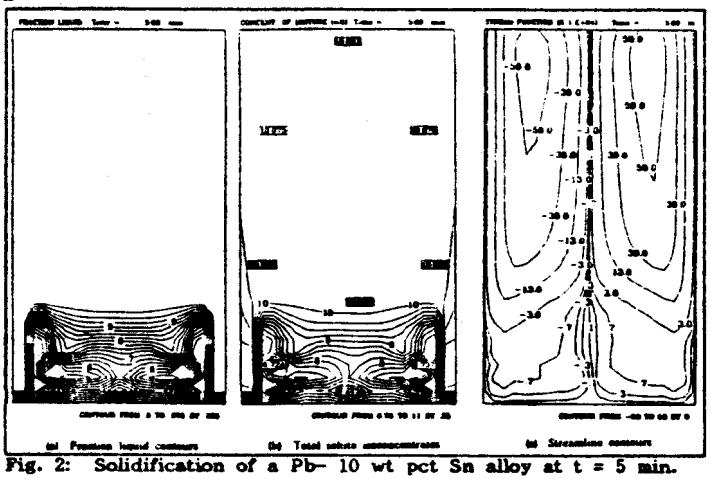

Fig. 2: Solidification of a Pb- 10 wt pct Sn alloy at t = 5 min.

The mold cavity is initially filled with a melt of Pb-10 wt pct Sn alloy subjected to a linear temperature distribution, varying from 577 K at the bottom to 586 K at the top (the initial thermal gradient is 10 K/cm). The container is 5 mm wide by 9 mm high. The side walls are insulated, and time dependent temperatures are imposed at the top and bottom according to

$$T_{hot} = 577 - 0.00833\ t$$
$$T_{top} = 586 - 0.00833\ t$$

where T is in K and t is time in seconds. This yields an initial solidification rate V = 7.78 x 10^{-4} cm/s and a cooling rate close to those in the experiments of Sarazin and Hellawell [5].

The first calculation considers an open top boundary, simulating an infinitely high container. No-stress conditions are imposed on the velocities at the top boundary, and no-slip on the other three boundaries. The calculation is carried on until the top of the mushy zone reaches about 80% of the container.

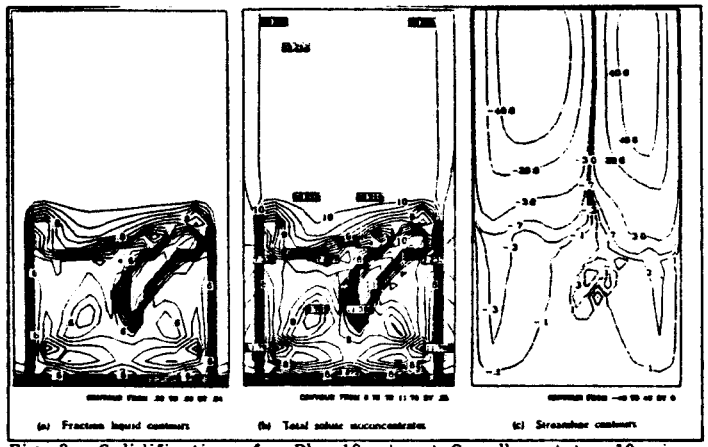

Fig. 3: Solidification of a Pb- 10 wt pct Sn alloy at t = 10 min.

The calculated results in Figs. 2a, 3a, and 4a clearly display long channel-shape penetrations of liquid regions into the mushy zone along the walls of the container. The liquid in these regions is flowing upward (Figs. 2c, 3c, and 4c) and is enriched in solute (Figs. 2b, 3b, and 4b), in agreement with experimental observations. Unsuccessful attempts of channel growth are also observed in the interior of the mushy zone, resulting in closed pockets of solute-rich liquid. Although the alloy is not yet completely solidified, it is evident that the concentration of the liquid in the channels increases with time. Because a higher concentration lowers the freezing point, these regions solidify last, and produce the localized solute-rich

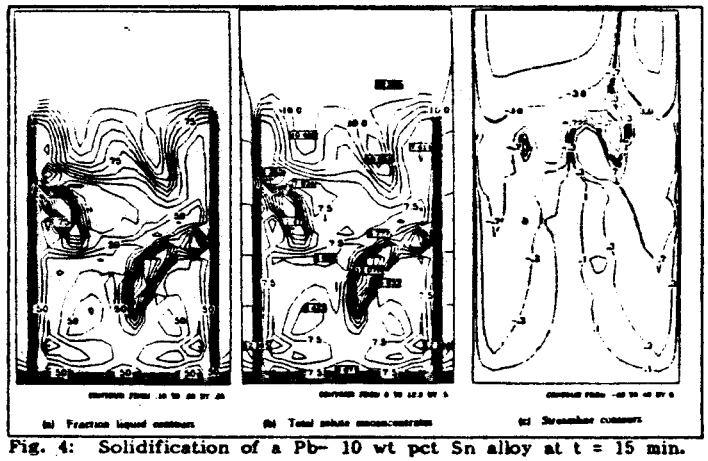

Fig. 4: Solidification of a Pb- 10 wt pct Sn alloy at t = 15 min.

freckles observed in the cross sections of castings.

This fact is confirmed in Fig. 5 which shows a completely solidified ingot, obtained by prescribing a zero vertical velocity at the top boundary so as to make the container finite. The cooling rate was doubled to 0.0167 K/s after 60 min of solidification, because by that time the mushy zone has reached the top of the container and the convection has greatly diminished. The alloy solidifies completely at t = 160 min. Figure 5 shows final composition of the casting, with evidence of strong segregation due to the channels along the walls, where the composition has reached about 27 wt pct Sn. Macrosegregation in the vertical direction along the interior part of the container is also observed, with compositions varying from a depleted bottom at about 4 wt pct Sn to a 12 wt pct Sn at the top. The pocketlike segregations observed during solidifications have also ended with higher concentration than the surrounding material. The strong positive segregation at the top of the mold is due to the accumulation of buoyant solute-rich liquid in this region during solidification. Because this is the last part of the cast to solidify, it has a high solute content.

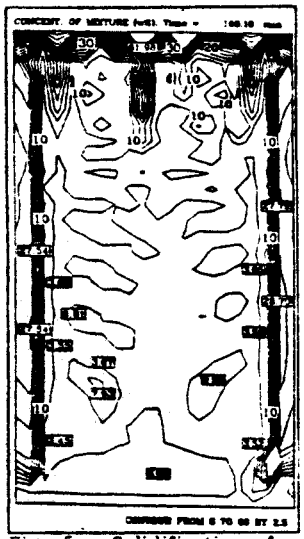

Fig. 5: Solidification of a Pb-10 wt pct Sn alloy. Final composition

CONCLUSIONS

A mathematical model of solidification of dendritic alloys with thermosolutal convection has been presented. The solidification is initiated from an all-liquid state, and the dendritic zone is allowed to grow as the volume fraction of liquid in the mushy zone adjusts according to local thermodynamic equilibrium conditions. Calculations were performed for the directional solidification of a Pb-10 wt pct Sn alloy, that reproduces channel formations and predicts severe segregation phenomena in castings. The prediction of channels in directional solidification is the first of its kind, and show the correct qualitative behavior observed in experiments [3-6].

The simulation of freckle formation is computationally very demanding. The exact simulation of a real experimental setting is severely limited by the high computational cost of resolving the small scales associated with freckles, in the relatively large solidification molds that are utilized in practice. A calculation in a small domain of dimensions 1 cm x 2 cm, with a 40 x 40 mesh, requires approximately 2 hours of CPU time in a Cray Y/MP8 per hour of solidification. The simulation of freckles in Sarazin and Hellawell's experiments [5] for example, with container dimensions of 4 cm (diameter) x 12 cm, would be prohibitively expensive. Furthermore, close quantitative predictions may require the use of 3-D models and a more general treatment of transport aspects, based on properly characterized thermophysical properties. Parallel computing will become essential to achieve this goal.

ACKNOWLEDGEMENTS

This work was supported by the National Aeronautics and Space Administration under Grant NAG 3-1060 and by Cray Research, Inc. and the San Diego Supercomputer Center. The authors are grateful for their sponsorship. The provision of financial support to S.D.F. by the Argentine Atomic Energy Commission is also gratefully acknowledged.

REFERENCES

1. McLean M., "Directionally Solidified Materials for High Temperature Service", The Metals Society, London, 1983.
2. Laxmanan V., Studer A., Wang L., Wallace J.F., and Winsa E.A., "Gravitational Macrosegregation in Binary Pb-Sn Alloy Ingots", NASA Technical Memorandum 89885, presented at the Low Gravity Science Seminar Series, University of Colorado, Boulder, Colorado, Feb. 17, 1986.
3. Copley S.M., Giamei A.F., Johnson S.M., and Hornbecker M.F., "The Origin of Freckles in Unidirectionally Solidified Castings", Metall. Trans., Vol. 1, 1970, pp. 2193-2204.
4. Sample A.K. and Hellawell A., "The Mechanism of Formation and Prevention of Channel Segregation During Alloy Solidification", Metall. Trans. A, Vol. 15A, 1984, pp. 2163-2173.
5. Sarazin J.R. and Hellawell A., "Channel Formation in Pb-Sn, Pb-Sb and Pb-Sn-Sb Alloy Ingots and Comparison with the System NH_4Cl-H_2O", Metall. Trans. A, Vol. 19A, 1988, pp. 1861-1871.
6. Tewari S.N. and Shah R., "Macrosegregation During Steady State Arrayed Growth of Dendrites in Directionally Solidified Pb-Sn Alloys", Metall. Trans. A, 1991, accepted for publication.
7. Flemings M.C. and Nereo G.E., "Macrosegregation: Part I", Trans. Metall. Soc., AIME, Vol. 239, 1967, pp. 1449-1461.
8. Ridder S.D., Kou S. and Mehrabian R., "Effect of Fluid Flow on Macrosegregation in Axi-Symmetric Ingots", Metall. Trans. B, Vol. 12B, 1981, pp. 435-447.
9. Bennon W.D. and Incropera F.P., "A Continuum Model for Momentum, Heat and Species Transport in Binary Solid-Liquid Phase Change Systems - I. Model Formulation", Int. J. Heat Mass Transfer, Vol. 30, 1987, pp. 2161-2170.
10. Beckermann C. and Viskanta R., "Double-Diffusive Convection During Dendritic Solidification of a Binary Mixture", Physico Chemical Hydrodynamics, Vol. 10, 1988, pp. 195-213.
11. Heinrich J.C, Felicelli S.D., Nandapurkar P., and Porier D.R., "Thermosolutal Convection During Dendritic solidification of Alloys: Part II. Nonlinear Convection", Metall. Trans. B., Vol. 20B, 1989, pp. 883-891.
12. Nandapurkar P., Porier D.R., Heinrich J.C, and Felicelli S.D., "Thermosolutal Convection During Dendritic solidification of Alloys: Part I. Linear Stability Analysis", Metall. Trans. B., Vol. 20B, 1989, pp. 711-721.
13. Heinrich J.C., Felicelli S.D., and Porier D.R., "Vertical Solidification of Dendritic Binary Alloys", Comp. Meth. Appl. Mech. Engng., 1991, accepted for publication.
14. Felicelli S.D., Heinrich J.C., and Poirier D.R., "Simulation of Freckles During Vertical Solidification of Binary Alloys", Metall. Trans. B, 1991, accepted for publication.
15. Felicelli S.D., "Simulation of Freckles During Vertical Solidification of Binary Alloys", Ph.D. Dissertation, University of Arizona, Tucson, Arizona, 1991.
16. Heinrich J.C., "A Finite Element Model for Double-Diffusive Convection", Int. J. Num. Meth. Engng., Vol. 20, 1984, pp. 447-464.
17. Heinrich J.C. and Yu C.C., "Finite Element Simulation of Buoyancy-Driven Flows with Emphasis on Natural Convection in a Horizontal Circular Cylinder", Comp. Meth. Appl. Mech. Engng., Vol. 69, 1988, pp. 1-27.
18. Heinrich J.C., "Numerical Simulation of Thermosolutal Instability During Directional Solidification of a Binary Alloy", Comp. Meth. Appl. Mech. Engng., Vol. 69, 1988, pp. 65-88.
19. Heinrich J.C. and Felicelli S.D., "Thermosolutal Convection During Dendritic Solidification of a Binary Alloy", in Finite Elements in Fluids, T.S. Chung, ed., Hemisphere Publishing Co. (in press).