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EFFECT OF BUOYANCY AND EXTERNALLY INDUCED FORCES ON THE SOLIDIFICATION OF BINARY MIXTURES

Final Report

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INTRODUCTION

Solidification occurs in a wide range of applications which include thermal energy storage, desalinization, welding, casting, and crystal growth. In each case successful implementation depends critically on proper control of transport processes in the liquid phase. For example, many modern electro-optical technologies place stringent requirements on the homogeneity of large, single crystals to which impurities (dopants) are added to achieve desired properties. However, when grown from a melt, release of the latent heat of fusion and compositional differences between the crystal and the melt cause the rate of growth and quality of the crystal to be strongly influenced by convection in the liquid. Just as convection may influence the structure and distribution of inclusions in a crystal, it can also lead to undesirable macroscopic constituent inhomogeneities, known as *macrosegregation*, in alloyed metal castings.

Convection in a solidifying system may originate from (i) external agents, (ii) the density difference between phases, (iii) surface tension gradients at a free surface, and/or (iv) the action of a body force on an unstable density gradient. Externally driven convection may, for example, be due to an imposed flow, rotational forces, and/or a magnetic field. Specific examples include the continuous casting of an ingot by withdrawal from a mold and crystal rotation in the Czochralski growth process. Density differences between the solid and liquid phases typically cause the mixture to contract during solidification, thereby inducing convection in the melt. Surface tension gradients at a free surface may arise from temperature and/or concentration gradients and may induce thermocapillary or diffusocapillary flows.

During dendritic solidification of an off-eutectic, multi-component system, density gradients result from both temperature and composition gradients, which may induce augmenting or opposing *buoyancy forces*. As determined by the equilibrium phase diagram, different solubilities of a component for the solid and liquid states dictate local component rejection or assimilation during phase change. Hence, during solidification, interdendritic fluid is depleted of its lighter or heavier component, causing its density to increase or decrease, respectively. Depending on the orientation relative to gravity, this *solutal* contribution to the liquid density gradient may enhance or retard the *thermal* contribution. If, for example, solidification occurs along a vertical boundary, the downward buoyancy force due to the horizontal temperature gradient may be opposed (or augmented) by the upward (or downward) buoyancy force due to the composition gradient. Bidirectional convective motions may result in the opposing case, while downward motion occurs in the augmenting case. In contrast, if a multi-component melt is frozen from below, rejection of a lighter component results in an unstable composition gradient which opposes the stable temperature gradient and may induce double-diffusive convection in the form of ascending and descending *fingers*.

Convection phenomena are complicated by the fact that, for an off-eutectic, multi-component system, solidification occurs over a temperature range which depends on composition. Due to dendritic growth, solid is formed as a permeable, crystalline-like matrix which extends into the liquid, creating a two-phase *mushy region* bounded by well defined solidus and liquidus isotherms. Fluid motion within the mushy region is coupled to convection in the melt and is the principal cause of compositional inhomogeneities in the final casting.

More specifically, large zones form, in which the solute concentration may be significantly greater or less than the intended composition. These zones are often referred to as *segregates* or *freckles*, and the phenomenon by which they form is known as *macrosegregation*.

Through the extent to which they offset or dampen thermo/solutal convection, external forces may be applied to reduce or eliminate macrosegregation. For example, in metals, which are electrically conducting, magnetic fields may be used to dampen convection by providing Lorentz forces which oppose fluid motion transverse to the magnetic field vectors. Alternatively, traveling magnetic fields may be imposed to vigorously stir the melt. In addition, for both metals and aqueous solutions, centrifugal forces induced by system rotation may be used to significantly alter fluid motion.

OBJECTIVES

Research performed under this contract originated with the premise that much could be done to improve existing techniques for modeling the effects of convection on solidification in mixtures by eliminating arbitrary characterizations of the mushy region and its coupling with the melt. It was therefore proposed that a set of continuum conservation equations be derived from the principles of classical mixture theory and that the model concurrently treat melt, mushy and solid regions as a single domain (a continuum). The conservation equations would accommodate all pertinent convection effects, and closure would be achieved by assuming local composition equilibrium at phase interfaces. The need for simplifying assumptions concerning the geometric regularity of the interfaces would be eliminated, along with the need for separately tracking the interfaces and using moving numerical grids and/or coordinate mapping procedures. Accordingly, specific objectives of the work have been to (i) develop models and procedures for simultaneously solving the coupled set of conservation equations which govern mass, momentum, energy and species transfer for solidification in a mixture, (ii) use the models to predict, as a function of time and over a representative range of operating conditions, velocity, temperature, and composition fields throughout solid, mushy and liquid regions of analog and metal alloys, (iii) validate model predictions by visualizing flows and performing temperature and concentration measurements under test cell conditions which simulate those of the computations, and (iv) delineate mechanisms responsible for macrosegregation and develop control strategies for its suppression.

RESULTS

Development of the continuum model is described by Bennon and Incropera (1987a, 1988a), and the first calculations were performed for an NH_4Cl-H_2O mixture in a closed rectangular cavity under transient conditions for which the lighter fluid (water) was rejected due to solidification induced at one of the vertical sidewalls (Bennon and Incropera, 1987b). The results yielded many of the robust features of binary solidification, which had either been known or surmised to exist from experiment. These features include the coupling of thermo/solutal buoyancy driven flows associated with the mushy and melt regions, establishment of a highly irregular liquidus front, and the formation of liquid pockets due to remelting in the mushy zones. Remelting facilitated the formation of channels in the mushy region, which, in turn, provided a preferential path for the advection of water-rich, interdendritic fluid to the liquidus front.

Calculations revealed, for the first time, conclusive confirmation of the relationship between channel flow occurring during the early stages of solidification and the formation of A-segregates in the final casting (Bennon and Incropera, 1987c). Additional calculations performed for an open rectangular cavity with throughflow (Bennon and Incropera, 1988b) and for a closed cavity with a free surface (Incropera et al., 1989) revealed the relative importance of mixed and thermo/diffusocapillary convection, respectively, on the solidification process.

Experimental studies of the solidification of an NH_4Cl-H_2O mixture in a rectangular cavity (Christenson and Incropera, 1989a) confirmed many of the foregoing features, as well as the initial development and subsequent erosion of double-diffusive interfaces in the melt. Subsequent computations performed specifically for the experimental conditions confirmed the observed double-diffusive phenomena (Christenson and Incropera, 1989b) but could not provide good quantitative agreement with all of the measured results. Experimental confirmation of important physical features without good quantitative agreement also characterized subsequent comparisons involving thermo/diffusocapillary and mixed convection flows (Engel and Incropera, 1989; Bennon and Incropera, 1989). Theoretical and experimental studies have also been performed to determine the effects of thermo/solutal natural convection on the solidification of a $NaCO_3$-H_2O solution in a horizontal, cylindrical (annular) cavity (Christenson and Incropera, 1989c; Neilson et al., 1990). Results have revealed a variety of rich and complex flow conditions, particularly with respect to double-diffusive layering in the melt.

In an effort to identify reasons for discrepancies between predicted and measured results, modeling techniques and data inputs have been systematically assessed. Since upwind differencing is known to be susceptible to artificially enhanced diffusion effects, this scheme was replaced by a power-law differencing formulation, which is known to attenuate the effects of false diffusion. However, differences between predictions based on power-law and upwind differencing schemes were found to be negligible. Moreover, the discrepancies could not be explained through the use of different, but physically consistent, permeability models for flow in the mushy region. A careful review of the accepted thermophysical property and phase diagram data base for the NH_4Cl-H_2O system revealed deficiencies which were corrected and yielded some improvement in the prediction of measured results, such as solidus and liquidus front locations. However, unacceptable differences in measured and predicted results still existed, and discrepancies were attributed to the fact that, in its original form, the model was unable to account for effects which have been observed experimentally and, in certain cases, may be first order. They include the existence of suspended particles, turbulent flow, and nonequilibrium effects (Christenson and Incropera, 1989a; Magirl and Incropera, 1993; Prescott et al., 1994b; Montgomery and Incropera, 1998).

Model improvements have subsequently been made to include the effects of nonequilibrium and suspended particles (Ni and Incropera, 1995a,b) and turbulence (Prescott and Incropera, 1995), as well as solidification shrinkage (Krane and Incropera, 1995, 1996) and a ternary (three-component) mixture (Krane and Incropera, 1997a,b). In addition, consideration has been given to alternative formulations of the mixture momentum equations (Prescott et al., 1991a).

Significant results have been obtained from theoretical and experimental studies of the unidirectional solidification (UDS) of NH_4Cl-H_2O from below. An impediment to application of the UDS process is a related macrosegregation phenomenon termed *freckling*. Upon examination of solids formed by UDS they are often found to be characterized by vertical, pencil-like segregates whose composition differs significantly from that of the surrounding material. If a cross-section of the solid is examined, the segregates appear as blemishes, or *freckles*, within a surrounding columnar crystalline structure. The freckles weaken the final product and are hence detrimental to any structural applications.

Application of the continuum model to UDS (Neilson and Incropera, 1991, 1992) has shown that, under conditions for which a compositionally induced density inversion develops in the mushy region and at the mush/liquid interface, a double-diffusive instability can occur at the interface. The instability yields a convection pattern characterized by colder, compositionally lighter fingers of fluid ascending from the liquidus into the melt, with adjoining fingers of warmer, compositionally heavier fluid descending to the liquidus. As solidification progresses, perturbations in field variables at the liquidus interface induce localized remelting of dendritic solid and the downward development of channels in the mushy region. The channels act as paths of least resistance for the transport of interdendritic fluid from the mushy region into the overlying melt and ultimately provide sites for freckle segregates in the final solid. The fully three-dimensional nature of these segregates has been computed (Neilson and Incropera, 1993a), and experiments have confirmed the double-diffusive convection phenomena and the development of channels in the mushy zone (Neilson and Incropera, 1993b). Modelling and experiments (Neilson and Incropera, 1993b,c) have also shown that, if a cylindrical mold is intermittently rotated about a vertical axis, Ekman boundary layers maintained at the liquidus interface during the start-up portion of the cycle essentially *wash* the interface of disturbances which contribute to channel formation. Hence, intermittent rotation provides a viable active control technique for improving the quality of UDS castings.

Theoretical and experimental studies have also been completed for metallic systems. For Pb-Sn (Presoctt and Incropera, 1991b) and Pb-Sn-Sb (Krane and Incropera, 1997a,b) alloys chilled at the sidewall of a mold, the continuum model has been used to determine the effect of cooling rate on thermosolutal convection and macresegregation. By increasing radial temperature gradients and hence the relative influence of thermal buoyancy, an increase in cooling rate renders the solutally driven interdendritic flows less able to penetrate the liquidus interface. Moreover, with increasing solidification rate, the permeability decreases more quickly within the mushy zone and fluid exchange with the melt is inhibited. With macrosegregation in outer regions of the casting (A-segregates) attributable to thermosolutal convection during early stages of solidification and cone segregates in the interior attributable to solutally driven convection during intermediate and later stages, the severity of macrosegregation decreases with increasing cooling rate. Experiments have confirmed some of the predicted trends but have also revealed distinct differences between experimental and numerical results (Prescott et al., 1994b; Krane and Incropera, 1998a,b). Differences were attributed to effects such as undercooling, recalescence, three-dimensional flow and solid particle transport, which were not considered in the model predictions.

Theoretical studies have also been performed to determine the extent to which application of a steady magnetic field can inhibit macrosegregation (Prescott and Incroepra, 1993). It was found that, for field strengths up to 0.5 Tesla, magnetic damping only impacted thermally driven flows during the early stages of solidification and that the overall effect on macrosegregation was small. This result was supported by scaling analyses, which indicated that magnetic damping is negligible relative to Darcy damping during intermediate and later stages of solidification. It was concluded that, if magnetic fields are to be effectively used for the control of macrosegregation, it would be through electromagnetic stirring (rather than damping), thereby requiring a time varying (a.c.), rather than a steady (d.c.), magnetic field. This premise was subsequently confirmed both theoretically (Prescott and Incropera, 1995) and experimentally (Prescott and Incropera, 1996).

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