The effects of convective flows on three-dimensional crystal growth patterns

Abstract

Experiments are proposed to study solidification of ammonium chloride from solution (analogous to casting of metallic alloys from a melt). The focus is on patterns carved out of the growing solid by convective flows. Long channels ("chimneys"), in particular, can make the material brittle and prone to fracturing. Several features make the current proposed research unique: (1) a high resolution, scanning imaging system will be developed to enable *three-dimensional* characterization of the growing solid; and (2) flows in the system will be *enhanced* artificially to clarify the role played by fluid flows in the pattern-formation process.

Significance and Plan of Procedure

There is tremendous interest in the solidification of ammonium chloride (NH_4Cl) from solution, since the patterns formed by growing NH_4Cl are similar to those formed when metallic alloys are hardened from a melt.[1] However, unlike metallic systems, NH_4Cl solutions are transparent, so the growing structures can be observed and measured quantitatively. Theories about the growth of NH_4Cl can be tested experimentally and extrapolated to common metallurgical processes. Crystal growth is also appreciated as an ideal system for testing theories of spontaneous pattern formation in dynamical systems far from equilibrium.

When an NH_4Cl solution is cooled below a critical temperature, solid NH_4Cl grows from the solution. The growth is rarely smooth and faceted, though; instead, needle crystals (dendrites) typically form.[2] In an extended system, the growing solid is characterized by a network of dendrites interspersed with small pockets of fluid.[3,4,5] This "mushy layer" is a porous medium through which the fluid can flow. The dynamics of the flows in the mushy layer are fascinating, because the flows themselves alter the dendritic network, dissolving the dendrites in regions with upward flows and enhancing solidification in regions with downward flows. The focus of this proposal is on the patterns that form due to this interaction between the flow and the solidification process.

There are several questions that this experimental research will address: (1) How and where do the mushy layer flows originate? Are they triggered by flows in the purely liquid region above,[6] or do they originate from within the mushy layer?[7] (2) What determines the size and density of chimneys (long channels) formed in the up-flow regions? (3) How are the chimneys affected by *enhancements* in the flows? This question is relevant for many realistic growth processes, where lateral temperature and compositional variations result in flows stronger than those present if the system is cooled uniformly from below. Also, by observing how the patterns respond to enhancements in the flows, we can better understand how, under normal circumstances, the patterns depend on the naturally-occurring flows. (4) What patterns are formed by *networks* of chimneys? How do these patterns depend on the imposed boundary temperatures? (5) What is the behavior of the patterns over time scales much longer than the chimney formation times? (6) Are there other structures that arise from the interaction between the flows and the solidification process?[8]

We have initiated experiments at Bucknell to address some of these question in a two-dimensional configuration. This geometry was chosen for the initial studies to simplify visualization of the solidification patterns. Novel techniques based on thermochromic liquid crystals are used to visualize the temperature field from which the flows can be inferred. In addition, the flows are enhanced either by tipping the apparatus (to produce horizontal density gradients) or with external pumping, and the resulting changes in the chimney properties (density and orientation) are measured. We have obtained evidence that slight enhancements in the mushy layer flows can *dramatically* increase the chimney density.[9]

The experiments proposed here will extend the current research program to include three-dimensional phenomena. To date, there are almost no *quantitative* experimental studies of large-scale dendritic growth patterns in a fully three-dimensional configuration, despite the fact that most real growth processes are three-dimensional. The three-dimensional studies will take advantage of the equipment and techniques that have already been developed. Using start-up funding provided by Bucknell University, we have assembled an image processing workstation based on a PC-compatible Unix workstation. Imaging boards (from Matrox Corp.) digitize, process and store video images from the experiment. We have written a general-purpose image processing program to control the image acquisition and analysis. Start-up funds have also enabled us to purchase temperature-controlled baths, three CCD video cameras, a peristaltic pump for external forcing of flows, an assortment of liquid crystal paints for temperature visualization, and other general purpose laboratory equipment (e.g., meters, camera equipment, etc.). During the next few months, we will also purchase (from start-up funds) a second computer for experimental control (and as a backup for the imaging workstation) and an additional Matrox frame grabber, along with a scientific-quality VCR.

Additional equipment will be required to implement three-dimensional visualization. We plan to generate a vertical sheet of light that can be aimed down on the growing solid and scanned across horizontally in discrete steps. At each step, the imaging system will digitize and store a video frame. The result will be a collection of images which, taken together, form a three-dimensional image of the interface. Major pieces of new equipment required include: (1) a mercury arc lamp with a paraboloid reflector to produce the illumination; (2) an optical table and a collection of optical supplies (mounts, mirrors, lenses, etc.) to manipulate the light into a sheet and aim it into the apparatus; (3) a stepper motor and controller with computer interface to scan the light sheet across the apparatus; (4) optical quality windows for the side-walls of the solidification apparatus; and (5) a re-writeable optical disk system to help us manage the enormous quantity of data that will be generated by this experiment (one run could easily generate over a Gigabyte of images).

In the second year of the grant, we plan to purchase a high-resolution (1340x1037) video camera. (The imaging boards already purchased can be interfaced to non-standard video cameras, so new boards will not be required for high resolution imaging.) This camera will double the precision of the images, enabling substantial improvements in the measurements. Another second-year enhancement involves characterizing the three-dimensional velocity and temperature fields. For this, the liquid crystal paints will be replaced by liquid crystal microspheres suspended in the flow. The colors of the microspheres reveal the temperature field, and the motions of these particles can be used to map the velocity field. During my post-doctoral fellowship in Texas, an undergraduate student and I developed computer programs -- using compatible Matrox imaging boards -- to track several dozen particles in a fluid flow. We will modify these program to enable three-dimensional tracking, using the scanning system developed during the first year of the grant.

An attractive aspect of the proposed research is its long-term potential. The issue of solidification in the presence of fluid flows will certainly not be exhausted in only two years. Furthermore, the solidification apparatus can be used to study long-term pattern formation in flowing systems with growing and dissolving boundaries (e.g., cave formations). Finally, the apparatus and scanning system can be adapted to study mass transport in three-dimensional flows, something that has not been done extensively in experimental systems.

The proposed research is ideally suited for undergraduate involvement. In fact, several undergraduates have already participated in and continue to participate in the research. Three students have played a major role in the development of computer programs to handle the image processing. A student worked in the lab last summer assembling the apparatus and taking preliminary data and is continuing this semester for independent study. Another student is working in the lab on a related experiment for his honor's thesis, and three students are scheduled to work in the lab this summer. During the grant period (and beyond) undergraduates will be involved in every aspect of the research, from development of the techniques, to data collection and analysis, to publication and presentation of the results.

Bucknell University excels among undergraduate institutions in its support of faculty and student research. In addition to providing start-up funding for my research, Bucknell has authorized $12,000 in matching funds for equipment funded by this proposal. Furthermore, Bucknell allows a one semester paid leave for untenured faculty in their third or fourth year to develop a research program. I have applied for and been granted my leave for the Spring of 1996. I have timed the submission of this proposal such that, if granted, it will begin at the start of my leave. I will therefore have eight continuous months at the beginning of the grant period devoted exclusively to research. Bucknell also supports research by providing funds for travel to conferences and routine day-to-day expenses (such as xeroxing, computer media, mailing, etc.) that at many institutions have to be requested in grants, and by providing free housing for students that do faculty-sponsored research during the summer.

Finally, it should be noted that the Physics department at Bucknell has just received a three-year NSF grant to support research for summer students (REU). I expect to be able to support one student each summer during the granting period through the REU program, so I have only requested funds to support one additional student each summer from Research Corporation.

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[1] See, e.g., McCay, M. H., McCay, T.D. and Hopkins, J. A., "The nature and influence of convection on the directional solidification of a metal alloy analog, NH_4Cl and H_20," Metallurg. Trans. B **24B**, 669 (1993).

[2] Mullins, W. W. and Sekerka, R. F., "Stability of a planar interface during solidification of a binary alloy," J. Appl. Phys. **35**, 444 (1964).

[3] Worster, M. G., "Natural convection in a mushy layer," J. Fluid Mech. **224**, 335 (1991).

[4] Chen, C. F. and Chen, F., "Experimental study of directional solidification of aqueous ammonium chloride solution," J. Fluid Mech. **227**, 567 (1991).

[5] Tait, S., Jahrling, K., and Jaupart, C., "The planform of compositional convection and chimney formation in a mushy layer," Nature **359**, 406 (1992).

[6] Chen, F., Ju, J. W. and Xang, T. L., "Convective instability in ammonium chloride solution directionally solidified from below," J. Fluid Mech. **276**, 163 (1994).

[7] Worster, M. G. and Kerr, R. C., "The transient behavior of alloys solidified from below prior to the formation of chimneys," J. Fluid Mech. **269**, 23 (1994).

[8] See, e.g., Braun, R. J., McFadden, G. B., Murrau, B. T., Coriell, S. R., Glicksman, M. E. and Selleck, M. E., "Asymptotic behavior of modulated Taylor-Couette flows with a crystalline inner cylinder," Phys. Fluids A **5**, 1891 (1993); for a more general discussion, see Glicksman, M.E., Coriell, S. R. and McFadden, G. B., "Interaction of flows with the crystal-melt interface," Ann. Rev. Fluid Mech. **18**, 307 (1986).

[9] We expect to publish these results this year.