DENDRITIC CRYSTAL GROWTH DYNAMICS

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ABSTRACT

With considerable NASA support, the scientific community has learned much in recent decades about the process of dendritic crystal formation, particularly as an example of steady-state pattern formation. Recently, efforts here and elsewhere have shifted towards the study of the time-varying aspects of the process. This paper will discuss the recent observations of the Transient Dendritic Solidification Experiment (TDSE). Data will be presented on the differences and similarities in the process by which two critical growth parameters, the growth rate and the tip radius of curvature, evolve as they approach steady state. This transient stage in the growth process is integral to many real-world industrial processes, and therefore a better understanding of it will serve as an important element of future industrial process models.

INTRODUCTION

Dendritic solidification is one of the simplest examples of pattern formation where a structureless melt evolves into a complex crystalline microstructure. Dendrites are known to occur in the solidification of water, salts, organic materials, and most commonly and importantly, in metals and alloys. There is considerable engineering interest in dendrites because of the role dendrites play in the determination of the physical properties of cast materials. In addition, dendritic solidification has become a well-studied model in the fields of nonequilibrium physics, and computational condensed matter physics.

Most theories of dendrite crystal formation consist of two components, the first concerns the transport of heat and solute from the solid-liquid interface into the melt. The second involves the interfacial physics that selects the unique growth velocity and tip radius of curvature from a spectrum of such possibilities that are consistent with transport and conservation of energy at the crystal-melt interface. Until recently, neither of these two aspects of the theory could be tested critically because of the effects of gravity-induced convection, which modifies the transport processes, and alters the growth kinetics.

Several of the authors of this letter participated in a series of experiments on the tip growth speed and radii of curvature of succinonitrile (SCN) dendrites grown in a convection-free, orbital-free-fall, environment. Our analysis shows that although theory yields predictions that are in reasonable agreement with these experiments, there were significant discrepancies, particularly in assessing interfacial pattern selection.

To better understand interfacial tip selection and stability, we are investigating transient and time-dependent dendritic growth by employing the relatively large Clapeyron pressure effect in SCN. A change in a solidifying system’s hydrostatic pressure changes the liquidus temperature, and induces a modification of the temperature gradients at the interface. With this approach, the kinetic behavior of isolated dendrites was measured as they evolved from one well-defined steady-state velocity at an initial supercooling, through a transient stage, to a different velocity at the altered pressure-supercooling conditions. By using fast pressure changes, the time-scale for pressure-related changes in growth behavior becomes well separated from the much slower thermal time-scale for long-range heat transfer.

PRESSURE AS A EXPERIMENT CONTROL PARAMETER

Background

The equilibrium melting temperature $T_m$ is the temperature at which the liquid and solid phases co-exist in equilibrium for some specified pressure. For most materials which contract upon melting (the well-known exceptions being water and silicon), increased pressure favors the crystalline phase, as atoms or
molecules are squeezed (on average), slightly closer together. This effect is classical, and can be derived from general thermodynamic principles and stated as the Clapeyron equation,

\[
\frac{\Delta T}{\Delta P} = \frac{T_v (v_s - v_l)}{\Delta h_f},
\]

where \(\Delta T\) is the change in melting temperature resulting from a small change in pressure, \(\Delta P\), \(v_s\) and \(v_l\) are the molar volumes of the liquid and solid phases, and \(\Delta h_f\) is the molar latent heat.\(^7\)

As such, the Clapeyron effect is well known in solidification science and for example has been hypothesized as the explanation for cavitation-induced nucleation. However, it is usually assumed that the Clapeyron effect is too small to be of interest in the solidification of metals and alloys. This may be a reasonable assumption for many materials, but it is not in the unusual case of SCN, which has a Clapeyron effect of 1.67±0.03 mK/psi.\(^5\) The Clapeyron effect in SCN is many times larger than in most metals. Moreover, the characteristic supercooling, the ratio of the latent heat to the specific heat, \(\Delta = \Delta h_f / c_p\), is approximately 23 K in SCN, which makes it many times smaller than that of metals and alloys. Thus, the ratio of the Clapeyron effect to the characteristic supercooling is 25 to 200 times larger for SCN than for typical metals. The large Clapeyron effect and the small characteristic supercooling may be employed to effect fast changes, and significant changes, in SCN’s crystal-melt equilibrium temperature.

Changing the interfacial temperature relative to the surrounding melt temperature changes the supercooling. This allows creation of a controlled non-steady-state set of dendritic growth conditions that permits observation of the growth kinetics during the transient evolution from an initial steady state to a final state.

If we subject an isolated SCN dendrite, growing at steady state at an initial supercooling, to a pressure-mediated melting temperature change, the dendrite will respond by growing in accordance to the new supercooling. To calculate this final supercooling properly, we need to account for the influence of any pressure-volume work done throughout the adiabatic crystal/melt system. From the combined first and second laws of thermodynamics, one can show that the adiabatic temperature change in the melt or the solid due to a pressure change can be written

\[
\frac{\Delta T}{\Delta P} = \frac{\beta T}{c_p},
\]

where \(\beta\) is the isothermal compressibility, and \(T\) is the absolute temperature prior to the pressurization. For SCN, the adiabatic temperature change in the melt has been measured by us to be 0.871±0.007 mK/psi, which is in reasonable agreement with the calculated value of 0.911±0.034 mK/psi made from published thermophysical parameters.\(^5\) Thus, by making a pressure change, we impose on SCN dendrites an effective net change in supercooling of approximately 0.80 mK/psi.

**Other Activity**

Experimental work by others that have employed a type of rapid temperature changes and observed the response of a dendrite include the use of heating the tip region of a dendrite with a modulated laser beam, or providing fluid flow changes near the solid-liquid interface.\(^8\)-\(^10\)

The major experimental challenge in measuring and analyzing transient and non-steady-state dendritic behavior is that it is difficult to repeat or characterize the initial and final conditions from which, and/or to which, a dendrite evolves. The proposed experiments in SCN described here attempts to obviate this difficulty by causing the transient or non-steady-state transition to occur between two well-characterized and repeatable sets of conditions. Sawada et al.\(^11\) have previously shown that pressure can indeed rapidly change crystal growth. They induced pressure-controlled solubility changes to examine crystal growth in a diamond anvil cell. More recently, Börzsönyi et al.\(^12\),\(^13\) have both grown 2-D dendrites in a liquid crystal, and simulated such growth with a phase field model, under oscillating pressure conditions.

**EXPERIMENT DESCRIPTION**

In the results reported here, we examine dendritic growth in SCN, a frequently and well-studied dendritic forming system, subject to a step change in pressure. To do this, we used a modified version of the apparatus used in the previously mentioned convection-free study of dendritic growth.\(^5\) In this setup the sample SCN is contained in a glass and stainless steel growth chamber, which is located within a precision (±2mK) temperature-controlled bath. The growth chamber interior volume communicates with the bath via a stainless steel bellows, permitting the controlled pressure in the bath to be transmitted into the chamber interior. We nucleate dendritic crystals through the use of the hollow stinger tube that penetrates the wall of the growth chamber. The exterior end of the stinger tube is capped and surrounded by a thermoelectric cooling element. The interior end is open to the chamber, allowing the sample material in the chamber to also fill the stinger.

During the operation of the experiment, we began each dendritic growth cycle by completely melting the SCN, and then lowering the melt’s temperature to the desired
supercooling. After the system reached the selected supercooled temperature, we activated the thermoelectric cooling element adjacent to the capped end of the stinger. This nucleated a small crystal in the interior of the capped end of the stinger, which then propagated down the stinger tube to emerge into the chamber as a freely growing dendrite. After the dendrite achieved steady state, we changed, as rapidly as we could, the hydrostatic pressure of the surrounding thermal bath via a pneumatically operated piston. The typical monotonic, roughly exponential, smooth pressure increase or decrease took about 2 to 6 seconds. The pressure was almost simultaneously transmitted to the sample via the bellows, producing the new operating conditions to which the dendrite needed to respond. Once a crystal emerged from the stinger, we recorded images of the growing dendrite from two perpendicular views, using both 35mm film and video cameras. The film cameras were set-up with black and white film, exposed by commercial xenon flash units, at an optical magnification of 2.27. The video cameras had imaging chip with an array of 640 x 480 pixels at 256 gray-scale levels, at an imaging rate of approximately 30 frames per second, and at an optical magnification of 0.46. This results in each pixel imaging a region of the chamber that is approximately 22.2 $\mu$m by 21.5 $\mu$m.

**EXPERIMENTAL RESULTS**

**The Morphological Transient Stage**

An increase in hydrostatic pressure is expected to result in an increase in the interface’s equilibrium temperature, an increase in the far field temperature, and a net increase in supercooling. This results in an increase in the temperature gradients, which enhances the solidification process, increasing the tip velocity and decreasing the tip radius of curvature. This is seen in the series of four dendrites edges extracted from photographs exposed every 14.5 seconds (Figure 1). The first two profiles at $t=0$ and at $t=14.5$ s are of tip radii of 46.8 and 46.5 $\mu$m respectively, both recorded at a supercooling of approximately 0.25 K, and prior to any change in pressure, growing with a tip interface velocity of approximately 17.3 $\mu$m/s. At $t=22.1$ to 24.1 s, the pressure changes to approximately 294 psi, which changes the supercooling to approximately 0.5 K. At $t=29$ s, about 5 s after the completion of the pressure change, the interface is more advanced then it would have been without the change, and the tip radius of curvature is about 31.9 $\mu$m. At $t=44.5$ s, the tip radius has become about 28.7 $\mu$m, and the tip velocity is between 50 to 60 $\mu$m/s as the far field temperature of the thermal bath drifts so that the supercooling is no longer steady and is between 0.5 and 0.6 K. The major difficulty is that by the time the first high spatial resolution photograph post pressure change (Figure 2) has been recorded, too much has happened without our observation. Nevertheless, as this 1st post-pressure photograph makes clear, even 5 s after the conclusion

![Figure 1: Time-laps of dendrite profile before, during, and after the stepwise pressure change. The pressure change occurs at approximately $t = 22.1-24.1$ s. $\Delta T$ correspondingly changes from 0.25 K to 0.5 K.](image1)

![Figure 2: High-resolution image (35mm film) of typical dendrite tip, obtained soon after the pressure change (within 5 seconds). The perturbations in the interface shape are evident (left and right sides) and the smaller tip has emerged.](image2)
of the pressure change, the dendrite is still in transition, and forms a sort of dendrite chimera where we see the head of a small-tipped fast-growing dendrite is attached to the body of a large-tipped slow-growing dendrite.

Because of the limited observations from the photographic data set, the comparison and examination of the transition region is best accomplished by an examination of the video data. Here we can observe the instantaneous and moving average velocity of the tip, and an approximate tip radius of curvature, at 30 fps as opposed to the approximately 0.07 photos per second discussed above. We analyzed the video images using a technique described previously three of the authors of this letter. This technique results in our ability to track the changing position of the tip to approximately 2 microns (~1/10 pixel). Limitations due to the spatial resolving capability of the current experimental setup prevent accurate, scaled measurements of the tip radius of curvature directly from video images. However, because of the potential value of high temporal data-rate $R$ information, we developed considerable effort and developed some methods to extract tip radius of curvature information directly from video data. This method suffers from the lower spatial resolution of the video as compared to the 35mm film, but still permits a more complete characterization of key dendritic growth parameters, $V$ and $R$, as they evolve and transition from the initial steady-state.

Departure From and Re-Acquisition of Steady State

We report now on another preliminary set of measurements from a data run that like the previous data has an initial supercooling of about 0.25 K, and is subject to an approximately 290 psi pressure change, resulting in a final supercooling of about 0.5 K. Again, the range of “final” supercoolings is due to the inability of current apparatus to adjust the outside of the chamber’s bath temperature to respond to the adiabatic warming due to pressure-work. The temperature of the surrounding bath does not change equally (due to different compressibility), which sets up a temperature difference between the sample and its surroundings that the temperature control cannot address quickly. This lack of control of the “final” supercooling limits the present studies more to how the dendrite “departs from the initial state”, rather than a rigorous observation on how it “approaches the new steady state”. Nevertheless, this limitation has not precluded useful observations from the experiments, like those discussed here.

![Figure 3: Typical dendrite tip radius of curvature, the tip velocity, the supercooling, and the pressure, all as a function of time.](image)
The data shows the tip radius of curvature, the tip velocity, the supercooling, and the pressure, all as a function of time (Figure 3). The units of tip radius are “arbitrary” since the methodology is still being validated (and clearly do not agree with the photographic data), but the time-variation of $R$ is valid. Here, the initial and final states are clearly identifiable, and with the time detail we now have, we see that the change in the radius lags behind the both the pressurization and velocity transition, which is completed well before the radius change begins to develop. In this case though, the transition times for both the radius change and the velocity change appear to be similar. We note an additional experimental difficulty in the dendrite tip location measurements needed for calculation of $V$. Immediately upon the pressure change, the dendrite was “shifted” in the images due to a mechanical flexing of a component of the optical path. We made a semi-quantitative correction in the displacement data where we have details of the changing pressure. Data that was not correctable by this method was not used, which is apparent as the small blank spot in the velocity-time data (Figure 3b).

The change in tip radius is also evident where the pressure change occurs is also evident in the low spatial resolution video images (Figure 4). Here one can see the difficulty in quantitative measurement as the dendrite in transition does not have enough of the emergent dendrite to apply standard tip radius measurement approaches. We also note that with closely spaced in time video images, we can demark the appearance of an anomalously large side branch, which was apparently instigated by the pressure change that created this transition.

**CURRENT & FUTURE ACTIVITIES**

At the present time, we are directing our efforts towards making improvements in our experimental apparatus’s capabilities. As discussed earlier, we currently have a limited ability to acquire both high temporal and high spatial resolution images simultaneously. The system currently being constructed will address this need. Additionally, the pressurization system will be updated to minimize the transition time, mechanically stiffen the apparatus (to better handle imaging during the pressure changes), and provide a more complete characterization of the pressure in the data record. The pressurization system will also provide a greater flexibility of control, such as sinusoidal (etc.) variations. These capabilities will permit a more careful study of the transient stage of the dendritic growth process including amplitude sensitivity, frequency and hysteresis effects. These data will be applied to improving our understanding of the side branch creation and amplification process.

Figure 4: A time sequence of 4 images showing the change in tip radius. This effect is also evident in the low spatial resolution video images (compare with Figures 1 & 2).
Eventually, these studies are intended to be conducted in the reduced-convection environment afforded in low earth-orbit. Such microgravity experiments will simplify the process by removing (or dramatically reducing) the natural convection in the melt. In such an environment, the system will no longer be compelled to establish a new convective fluid flow pattern when the supercooling is changed. This would reduce the process to strictly diffusive heat transfer and local interfacial processes. Despite this important need, it presently appears that due to limited resources, microgravity experiments such as this are likely to be postponed beyond the foreseeable future. In the meanwhile, ground-based experiments will continue, which provide the investigator team with an opportunity to develop the apparatus further and generate a more comprehensive description of the process.

SUMMARY & CONCLUSIONS
These observations further suggest the potential for using pressure change both to better understand the phenomena of interfacial stability, side-branch formation, and the so-called “selection” process in dendritic growth theory, and as a way to use pressure steps or oscillations to control or engineer dendritic microstructures.

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