Study of Solid-Liquid Interfaces during Solidification, Using Ultrasonic Waves

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We have studied the onset and evolution of instabilities at the solid-liquid interface of tin undergoing directional solidification, as a function of growth velocity, temperature gradients, and impurity content. The initiation of an instability that we identify as "cellular" growth, and its passage to pseudosteady state, have been investigated. Within this steady state a new oscillatory phenomenon has been found, indicative of changes in the interface configuration that are quasiperiodic in time.

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An understanding of solidification phenomena such as the kinetics of the solid-liquid interface (hereafter SLI) and SLI topography, that leads to the rich and complicated solidification patterns, is of long-standing interest.[1-4] Among the most intriguing and not yet fully understood are the SLI instabilities and resulting structures, such as "cells" and dendrites, that develop under highly nonequilibrium solidification conditions. It is also noted that the instability which results in cellular solidification bears a strong similarity to the Bénard instability that leads to the development of convection patterns in a fluid. However, in the case of solidification, experimental studies of these processes are often hindered by the difficulty of observing the SLI while it is moving, especially in optically opaque substances.

We have undertaken, therefore, to investigate the features of the advancing SLI, in directional solidification, by means of ultrasonic waves that propagate from the liquid to the SLI, in the manner shown in Fig. 1. (A preliminary description of this work appeared in Suzuki, Hikata, and Elbaum.[5]) This approach allows us to follow the SLI in real time and to monitor continuously the development of instabilities. We note that use of ultrasonic waves for observing solidification or melting has a long history. A brief survey on this can be found in an article by Parker.[6]

Tin, nominally 99.99% pure, was melted in a crucible, then directionally solidified from the bottom up through contact with a cooling rod (Fig. 1). Concurrently, pulsed ultrasonic waves (pulse width $\simeq 5$ μs, pulse repetition rate $\simeq 100$ s^{-1}) were propagated from the transmitting-receiving transducer and the echoes reflected from the SLI were monitored for changes in amplitude. These changes are determined to within ± 0.05 dB. Measurements of the transit time of the waves in the liquid (between the transducer and the SLI) were used to determine the location and velocity of the SLI. The ultrasonic frequency used was 5 MHz most of the time, with a few experiments carried out with 15-MHz waves; analogous results were obtained for both frequencies. The average temperature gradient in the liquid was measured with a thermocouple located at an adjustable position relative to the SLI, as indicated in Fig. 1. To determine the effect of impurities on the phenomena under study, additions of 0.05 and 0.2 at% lead were made to the liquid and the same types of experiments were repeated. The temperature gradients used ranged from 6 to 12 °C cm^{-1} and the average growth rates ranged from 1.6×10^{-4} to 10^{-3} cm s^{-1}.

The results obtained for the onset of an instability at the SLI and passage to a new quasisteady state are shown in Fig. 2. In the figure the average amplitude of the ultrasonic echoes reflected from the SLI (normalized to the amplitude at the smallest growth velocity used) is plotted as a function of G/R; here G is the temperature gradient in the liquid and R is the growth rate (velocity of advancing SLI). The data shown are for two fixed values of the temperature gradient G, as well as for two values of impurity content, i.e., 0.01 (impurity unknown) and 0.05 at.% of lead. At small R, the interface is ex-

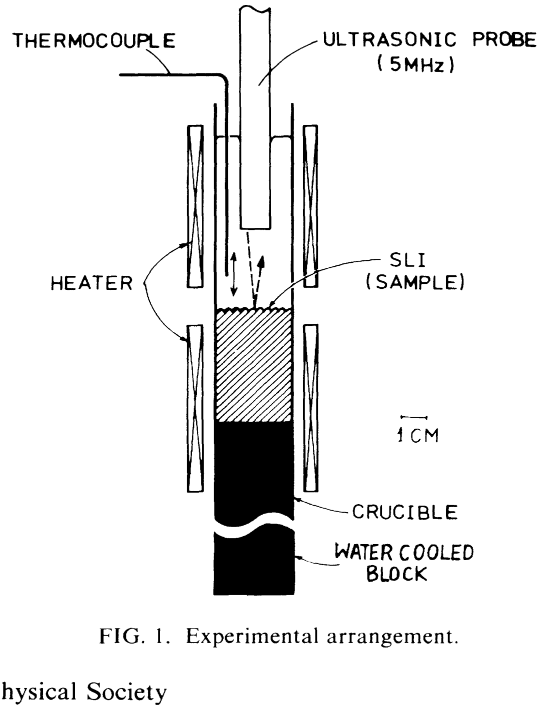

FIG. 1. Experimental arrangement.

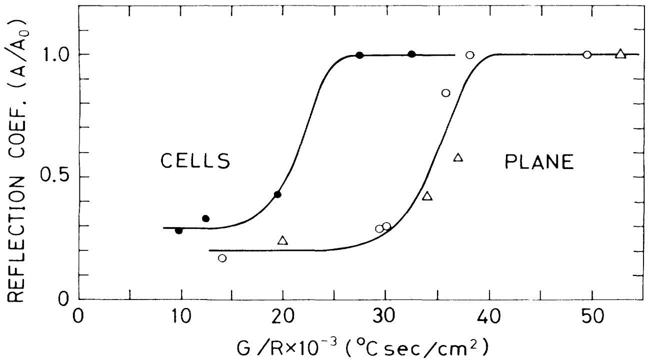

FIG. 2. Averaged amplitude of ultrasonic waves reflected from the solid-liquid interface as a function of G/R. Filled circles: tin 99.99% pure, temperature gradient $G=6.45\ ^\circ\mathrm{C\ cm}^{-1}$; open circles: tin plus 0.05 at.% lead, $G=6.45\ ^\circ\mathrm{C\ cm}^{-1}$; triangles: tin plus 0.05 at.% lead, $G=12.0\ ^\circ\mathrm{C\ cm}^{-1}$.

pected to be flat, at least on the scale of the wavelength of the propagating sound wave. Thus, for a given attenuation in the liquid, the received signal (i.e., echoes reflected from the SLI) is expected to be determined by the value of the sound reflection coefficient at the SLI (we note that this coefficient is small, since the difference between the acoustic impedances of the solid and liquid is small). For displacements of the SLI that are small compared with the wave path x in the liquid (x is typically 4 cm), the signal amplitude should be essentially independent of SLI position. As seen in Fig. 2, a constant received (i.e., reflected from the SLI) amplitude is indeed observed for small R. As R reaches a certain critical value, the signal amplitude begins to decrease and eventually reaches a new level, typically with a total drop of a factor of 3 to 5 (a decrease of 8 to 14 dB). Since the bulk acoustic impedances of the solid and liquid remain unchanged, this decrease in amplitude must be due to scattering of the waves from geometric irregularities that appear at the interface. We identify, therefore, the start of the decrease in amplitude as the onset of cellular growth caused by the development of an instability known as constitutional supercooling,[7] and the lowest-amplitude (high velocity) regime as the fully developed cellular structure. The transition from the initially flat to the fully cellular SLI occurs over a range of R and thus over a time interval that depends on the imposed rate of velocity change. We also measured the effects of increasing the impurity concentration in the liquid at a fixed temperature gradient and that of increasing the temperature gradient at the SLI for fixed concentration. These changes are found to cause, respectively, a decrease and an increase of the critical velocity for the occurrence of the instability. These results are consistent with the expectations of the model of constitutional supercooling and agree qualitatively with earlier reports.[1-3]

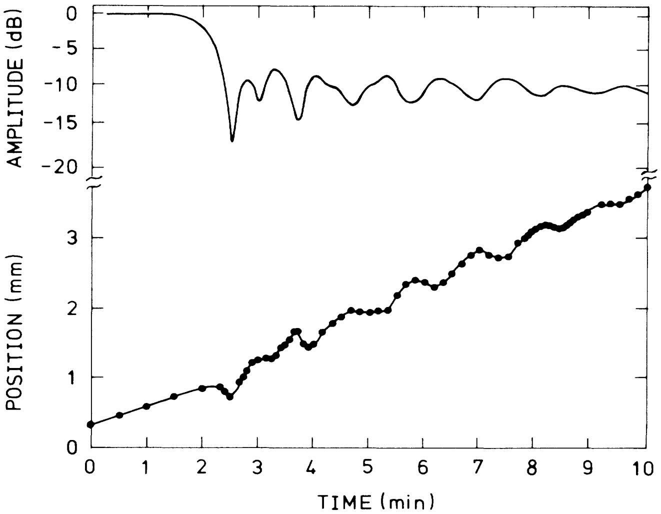

FIG. 3. Unaveraged amplitude of ultrasonic waves reflected from the solid-liquid interface (top), and of solid-liquid interface position (bottom), both as functions of time. Material: tin 99.99 at.% pure; $G=6.45\ \mathrm{C\ cm}^{-1}$.

We note, however, that in our work the onset of instability is observed at lower impurity concentration, for a given value of G/R, than in previous studies. We attribute this result to greater sensitivity of our technique. Indeed, in earlier work[8,9] the results were obtained by decantation of the liquid and examination of the SLI under a microscope, after cooling. In this procedure a thin layer of liquid, usually retained on the interface during decanting, freezes afterward and masks the early (fine) features of the instability.

In the course of these studies we found a new phenomenon shown in Fig. 3. In this figure we present unaveraged amplitude of the echoes reflected from the SLI and the position of the SLI, both as a function of time. As is readily seen, following the initial portion of constant amplitude and its subsequent drop, the amplitude of the ultrasonic reflected signal goes into quasiperiodic oscillations in time. The interface position also goes into oscillations with the same period, while advancing monotonically on average. The observed oscillations indicate the presence of an unexpected quasiperiodic variation in the cellular structure of the SLI. This periodic variation does not appear to be a part of existing models and is thus a new feature of solidification instabilities.

These oscillations are tentatively interpreted as generated by a relaxation oscillation involving quasiperiodic variations of constitutional supercooling (CS) at the SLI, with characteristic times τ_1 and τ_2. This phenomenon can be described qualitatively as follows. When the factor G/R reaches a value appropriate for CS to develop, the SLI becomes marginally unstable. As the CS increases, SLI fluctuations develop resulting in the formation of cells that tend to eliminate the CS. This elimination is further enhanced by the lateral diffusion of impurities, away from the tip of the advancing cell [see Fig. 4(a)] and into the intercellular spaces. Eventually, the cell tip reaches a region in the liquid of temperature and composition that no longer supports the average growth rate. At the same time the additional accumulation of impurities in the intercellular spaces will depress the freezing temperature, thus altering the CS, and may even cause transient remelting (see Fig. 3). For remelting to happen impurities must migrate the depth of the groove in a time t_1 that is shorter than the time t_2 taken by the temperature distribution (moving with the imposed average R) to advance the same distance. Approximate estimates of these numbers can be obtained as follows. Use of typical values of the diffusion coefficient in the liquid of $D \simeq 10^{-5}$ cm^2 s^{-1}, and cell depth $d \simeq 2\times10^{-2}$ cm, gives $t_1 \simeq d^2/D = 40$ s. This value of t_1 is to be compared with t_2 corresponding to the average growth rates, R, used when oscillatory behavior is observed, i.e., $2.5\times10^{-4} \simeq R \simeq 10^{-3}$ cm s^{-1}. Thus $t_2 \simeq d/R$ covers the range $\simeq 30$ to 120 s, which clearly straddles the estimated value of t_1. This is consistent with the experimental results, as shown in Fig. 3, where the interface position is seen to be receding over a portion of most periods. Occasionally the interface remains stationary for part of the period, as seen in Fig. 3 between $\simeq 3$ and $\simeq 3.3$ min. In view of the approximations used in estimating t_1, one would expect that whether remelting occurs might depend in a sensitive way on the local values of other growth parameters, such as the temperature gradient, G. Eventually, as the interface temperature is lowered, growth resumes and the intercellular regions "fill in" with solid, thus reducing their depth and effectively bringing the SLI closer to a flat configuration [Fig. 4(b)]. This change in geometric configuration reduces the lateral diffusion, and impurity accumulation ahead of the cell tips is again enhanced. CS thus again develops, the growth rate of the tips is increased, they become elongated [Fig. 4(a')], and the cycle repeats. This is consistent with the observation that the amplitude minima of the ultrasonic wave (corresponding to maximum scattering, and thus to the longest protrusions from the interface) generally occur at the end of the most rapid growth part of the cycle, as seen in the displacement versus time plot of Fig. 3.

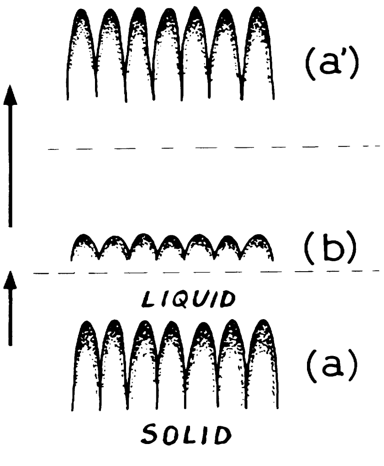

FIG. 4. Schematic cross section of solid-liquid interface. (a),(a') fully developed cellular protrusions; (b) partially suppressed cellular protrusions (see text).

The relevant time constants of these processes can be estimated and compared with the observed quasiperiods. The time τ_1 required for CS to develop is of the order of impurity (solute) diffusion time in the liquid over a distance of the order of a cell depth, calculated above as $t_1 \simeq \tau_1 \simeq 30$ s. This value is to be compared with the experimentally observed quasiperiods of oscillation ranging from 30 to 90 s. Under the conditions of oscillatory growth observed here, the time τ_2 for an interface perturbation (protrusion) to advance into a region of CS is expected to be shorter than the value given by the average R. It is difficult to estimate τ_2, except with reference to our experimental results (Fig. 3), where we identify with τ_2 a portion of the largest-positive-slope region of the cycle in the curve of position versus time. This corresponds to the rapid growth of protrusions, as discussed above.

Parker and Manning[10] presented a series of photographs of ultrasonic echoes reflected from the solid-liquid interface of tin during solidification and melting. The interface is set in motion by rapid movement of the crucible to a new position with respect to the furnace. The photographs are taken at 60-s intervals on the same film. From these photographs two things are apparent: (a) The height of the echo is changing more or less randomly as the echo advances toward the new equilibrium position, i.e., there seems to be a quasioscillatory characteristic in the echo amplitude. (b) The advancement of the echo position is not monotonic in time, i.e., there are accelerations and decelerations in the motion. Although these observations have not been mentioned in their article, the results might be related to the phenomena described in this paper.

In another study, Parker, Manning, and Peterson[11] discussed variations of ultrasonic reflections from the SLI arising from (a) wave interference due to geometric effects, and (b) "mashy" interfaces encountered in the solidification of alloys. We note that neither of these causes applies in the present case.

In summary, we have studied the behavior of the solid-liquid interface of a directionality solidifying metal, using ultrasonic waves. We have identified the transition from a flat to a cellular interface. We observed a new mode of growth that is oscillatory and quasiperiodic in time. We interpret these results in terms of relaxation oscillations.

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