



# Dynamics of planar interface growth during directional solidification of alloys

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The dynamics of plane front growth during directional solidification is investigated in a well-characterized system of succinonitrile–acetone, and the results show significant deviations from the predictions of existing models. This discrepancy is shown to arise from the assumption of solidification from one end in the theories that ignore the presence of an initial solute boundary layer generally present in experiments. A numerical model that relaxes this assumption is presented that gives excellent agreement with the experimental results.

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During directional solidification of alloys, the solidification dynamics go through an initial transient before a steady state is established. During this initial transient, a solute boundary layer gradually develops next to the interface due to the imbalance between the rate of rejection of solute from the interface and the rate of diffusive transport away from the interface. For solidification conditions that give rise to a diffusion-controlled stable planar interface growth, the solute build-up initially increases during the transient regime, then remains constant when the planar interface reaches the steady-state growth condition, and finally increases as the end of the sample is approached. A quantitative understanding of the initial transient is important for many solidification and crystal growth processes. For example, in order to produce crystals with uniform composition, it is important to determine the length of the sample that is growing under steady-state growth conditions with uniform composition in the solid since the initial and final transient lengths can be significantly large under the low growth rate conditions required for planar front growth. The measurement of the solute profile in the crystal during the transient time, and its comparison with the diffusion-limited model, may indicate any departure from pure diffusion-controlled growth mode and the existence of non-equilibrium effects at the interface or the presence of convection in the liquid. A precise characterization of the initial transient is also

critical in establishing the planar interface instability condition since in real systems the interface becomes unstable before reaching the steady-state condition.

A simplified conceptual model to predict the transient composition profile in solids for a planar interface growth was first proposed by Tiller et al. [1] and a detailed mathematical analysis was subsequently given by Smith et al. [2] for diffusive growth conditions. These models are approximate in that they assume that the solid–liquid interface velocity is precisely equal to the pulling velocity from the very beginning of the solidification (i.e. at  $t=0$ ). This implies that the interface response time to the change in the external velocity is exactly zero. In an actual directional solidification experiment, the interface velocity does not instantaneously rise from zero to the externally imposed velocity and this variation in interface velocity significantly influences the rate of solute build up in the liquid and the resulting composition profile in the solid. The constant-velocity model also has a drawback in that it does not show the effect of temperature gradient on the solute profile in the solid during the transient time. Since the interface moves from near the liquidus to the solidus isotherm during the transient, the imposed temperature gradient must influence the transient dynamics.

A significant insight into the dynamics of solute build up ahead of a transient growth of a planar interface was first obtained from the model of Warren and Langer (WL) [3], which used the integral method for the solution of partial differential equations originally developed by Theodore von Karman [4,5]. Subsequently, Caroli et al. [6] developed

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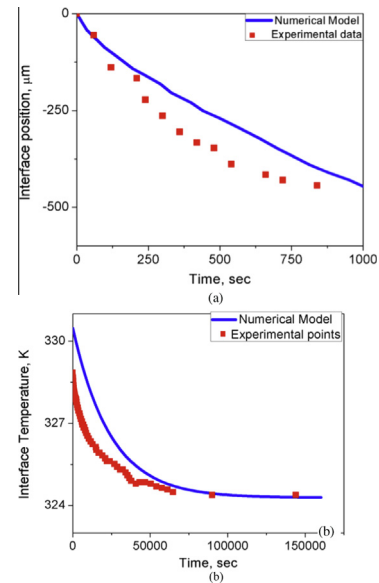
an analytic al model using the Green function method, and Coriell et al. [7] developed a numerical model for the initial transient. All these models relaxed the assumption of initial velocity to be equal to the imposed velocity, but retained the assumption of no diffusion in the solid, no thermal lag in the system and uniform composition in the liquid at the start of solidification.

Although detailed models of initial transient have been proposed, experimental studies have not been conclusive due to the presence of convection [8] or due to lack of independent evaluation of system parameters [9]. The major aim of this paper is to present the results of benchmark experimental studies that quantitatively investigate the transient behavior in thin rectangular samples of succinonitrile (SCN)–0.23 wt.% acetone in which convection effects are negligible, and all relevant parameters of this system are accurately known and measured independently so that no free parameter is needed to fit the model based on diffusive growth conditions. Experimental results are found to deviate significantly from the predictions of the existing models, and the deviation is observed to increase as the thermal gradient is increased. This deviation is evaluated by comparing the experimental results with a numerical model [10] that allows us to relax the assumptions of the existing models.

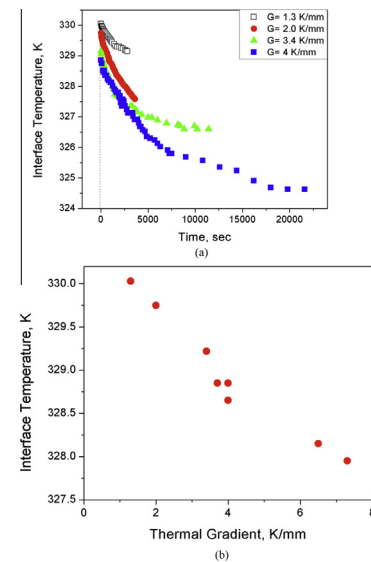
The experimental procedure, sample preparation, interface position and interface temperature measurement technique used in this study are identical to those described by Xu et al. [11], and therefore will not be repeated here. The sample was held in the thermal gradient stage for some time to obtain thermal equilibrium and when the interface appeared to remain stationary the sample was directionally solidified at a fixed imposed velocity. The temperature of the interface was characterized as a function of time, including  $t = 0$ , when the directional solidification run was started. Experiments were carried out for two different velocities and four different thermal gradient values, and the position of the interface and the temperature of the interface as a function of time were measured experimentally for each experiment.

The interface position as a function of time for  $V = 2.25 \mu\text{m s}^{-1}$  and  $G = 3.8 \text{ K mm}^{-1}$  is shown in Figure 1a along with the predictions of existing theoretical models [3,6,10], and a significant deviation is observed. Similar discrepancies were found at other experimental conditions. To obtain an insight into this deviation, the interface temperature as a function of time was also measured, and the results for an experiment with  $V = 1.0 \mu\text{m s}^{-1}$  and  $G = 4.0 \text{ K mm}^{-1}$  are shown in Figure 1b; these also show significant disagreement between the theoretical predictions and experimental data. However, an important observation is made in that the initial temperature of the stationary interface is not at the liquidus temperature, as assumed in all theoretical models, which indicates that the initial composition in the liquid is not uniform and a small boundary layer of solute is present in the liquid at the interface. To examine the effect of thermal gradient on the initial interface temperature, experiments were carried out for four different temperature gradient values and the results are presented in Figure 2a. The initial interface temperature was found to decrease with an increase in the thermal gradient value, as shown in Figure 2b, which is in contradiction to the theoretical assumption that the initial interface will be at the liquidus temperature for all temperature gradient values.

We now evaluate the reason for the deviation of experimental results from the predictions of the current theoretical models so that a proper model can be developed to



**Figure 1.** (a) The variation of interface position with time for  $V = 2.25 \mu\text{m s}^{-1}$  and  $G = 3.8 \text{ K mm}^{-1}$ , and (b) the variation of interface temperature with time for  $V = 0.75 \mu\text{m s}^{-1}$  and  $G = 3.7 \text{ K mm}^{-1}$  in SCN–0.23 wt.% acetone. Experimental results are shown as circles, and the corresponding results of the theoretical model that assumes initial uniform composition  $C_0$  in the liquid are also shown for comparison.

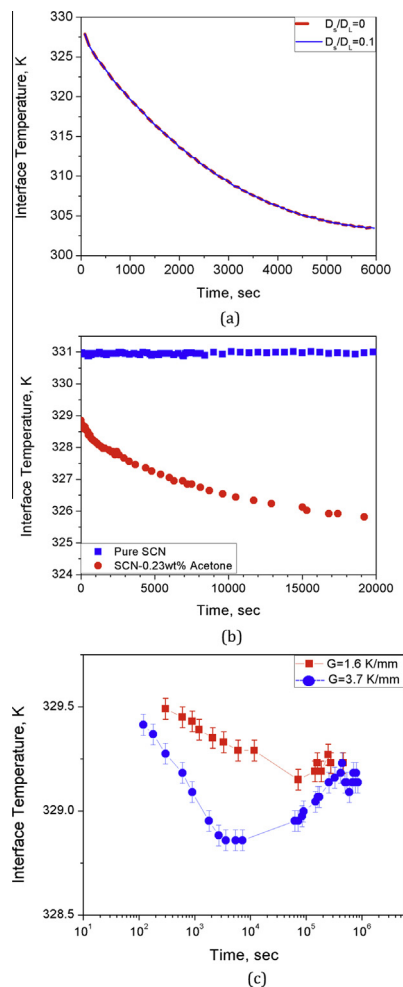


**Figure 2.** (a) Interface temperature as a function of time in SCN–0.23 wt.% acetone for  $V = 1.0 \mu\text{m s}^{-1}$ , and  $G = 1.3, 2.0, 3.4$  and  $4.0 \text{ K mm}^{-1}$ . (b) Temperature of the initial stationary interface as a function of imposed thermal gradient.

characterize the initial transient during the directional solidification process. We use a finite-difference model based on a fixed frame of reference [10], which will allow us to relax different assumptions in the existing models. We shall examine three key assumptions of all current models, which are: (i) the diffusion in the solid is negligible; (ii) the isotherms move instantaneously with the pulling speed so that no thermal lag is present in the system; and (iii) the composition in the liquid is uniform initially at the start of solidification and is equal to the initial composition of the alloy or the interface temperature is at the liquidus temperature of the alloy.

To investigate the effect of diffusion in the solid on the development of the composition profile in the solid, a set of computations was done with  $C_0 = 1.0$  wt.%,  $G = 10.0$  K  $\text{mm}^{-1}$ ,  $V = 3.0$   $\mu\text{m s}^{-1}$ ,  $D_\ell = 1.27 \times 10^{-9}$   $\text{m}^2 \text{s}^{-1}$  and  $k = 0.2$ . The effect of diffusion in the solid at the interface where the flux of solute enters the solid will reduce the rise in composition and give a slightly lower composition. Figure 3a shows that diffusion in the solid does not significantly influence the variation in interface temperature so that our measured interface temperature profiles are not influenced by the diffusion in the solid.

We now examine the assumption in the model that the interface moves instantaneously once the sample is moved in the thermal gradient stage. Since the interface recoil during growth can come from both the thermal and the solute transient effects, it is necessary to separate these two effects to accurately determine the effect of thermal lag. The thermal recoil in thin samples was investigated by directionally solidifying pure SCN to avoid the solute effect on the transient. Figure 3b shows the results for the interface temperature vs. time during the growth of pure SCN and SCN–0.23 wt.% acetone alloy. In pure SCN the initial



**Figure 3.** (a) The effect of diffusion in the solid on the interface temperature. (b) Interface temperature as a function of time after the initiation of directional solidification for pure SCN and SCN–0.23 wt.% acetone showing absence of thermal lag. (c) Interface temperature as a function of time for thermal gradient values of 1.6 and 3.7 K  $\text{mm}^{-1}$  at  $V = 0$ , SCN–0.23 wt.% acetone.

stationary interface was at the melting point of pure SCN, and the interface remained at that temperature as the sample was solidified so that neither thermal lag nor interface kinetic effects are present in the system.

We now examine the basic assumption made in all existing theoretical models of directional solidification transient that the sample is solidified from one end so that solute concentration is uniform in the entire liquid at the start of solidification ( $t = 0$ ) and the interface temperature is exactly at the liquidus temperature of the alloy. In practice, the most common procedure is to place the sample in the thermal gradient zone with part of the sample remaining solid. Some solid is required to be present when a seed crystal is used to select the orientation of the crystal. Also, if the sample is melted completely and solidified from one end, the thermal profile will not be steady state initially so that some thermal transient will be present and the assumption of frozen thermal gradient will not be valid. The development of solute boundary layer during the time the sample is held stationary in the thermal gradient stage was recently demonstrated by Xu et al. [11], who examined in detail the interface dynamics in SCN–0.25 wt.% camphor for one thermal gradient value with no imposed velocity. Experiments, similar to those described by Xu et al. [11], were carried out in SCN–0.23 wt.% acetone for two different thermal gradient values since the experimental results in Figure 2b show a strong effect of thermal gradient on the initial interface temperature. The variation in interface temperature with time is shown in Figure 3c, which shows a similar behavior as described by Xu et al. [11], except that the variation in interface temperature with time was found to depend on the value of the thermal gradient. The minimum in temperature is decreased, and occurs at a smaller time, as the thermal gradient is increased. The decrease in interface temperature initially occurs as the interface compositions in the liquid and solid are change to satisfy the local equilibrium condition at the interface. However, some liquid droplets of higher composition are present in the solid behind the interface that move towards the interface due to the presence of thermal gradient and become incorporated into the liquid, thereby increasing the liquid composition at the interface and decreasing its temperature [11,12]. The maximum in composition or the minimum in interface temperature occurs when all the droplets have disappeared from the solid so that its value depends on the rate of droplet migration, or the value of the thermal gradient. Once all the droplets are removed from the solid, the boundary layer relaxes and interface temperature increases to approach a constant value that is independent of the thermal gradient and is below the liquidus temperature. For  $G = 1.6$  and 3.7 K  $\text{mm}^{-1}$ , the interface temperatures after a long time are 56.1 and 56.0 °C; these values are similar and hence do not depend on the temperature gradient value, but are significantly lower than the liquidus temperature of 57.44 °C for this alloy composition, showing the presence of a solute boundary layer in the liquid.

In most experiments, the sample is held stationary in the thermal gradient stage until the motion of the interface is negligible over a significant time period. In our experiments the minimum in the interface temperature is shallow, Figure 3c, so that the interface visually appears to be stationary near the minimum and the directional solidification was started near this minimum temperature, which explains the observed effect of thermal gradient on the initial interface temperature, as shown in Figure 2b.

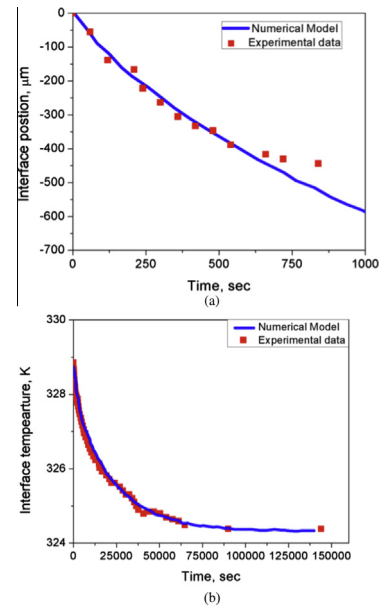
Experimental studies of directional solidification in which the sample is first placed in the thermal gradient zone to stabilize the thermal field show the existence of a solute boundary layer that must be taken into account in the theoretical models of the initial transient. Losert et al. [9] have carried out detailed experiments on the initial transient in the SCN–coumarin system, and found a good agreement with the WL model without considering the presence of an initial boundary layer of solute in the liquid. This is because the liquidus temperature of this composition was not known independently, and Losert et al. assumed it to be equal to the temperature of the solid–liquid interface in the thermal gradient zone after stabilization for 2 days. Since the interface temperature should be below the liquidus temperature, as observed in Figure 3c, they have effectively considered a slightly higher composition of the alloy that somewhat compensates for the solute in the boundary layer.

Once the presence of an initial boundary layer is established, the theoretical model can be modified by replacing the initial boundary condition of constant composition in the liquid with the initial solute profile present in the liquid. Since the interface temperature variation with time during planar interface growth is not influenced by the diffusion of solute in the solid, Figure 3a, one only needs to consider diffusion in the liquid for the characterization of the subsequent interface dynamics when the sample is moved for directional solidification. One of the simplest ways to include the presence of the initial solute profile in the model is to use the existing model of the initial transient in which the growth is assumed to occur from the initially uniform composition in the liquid, and then determine the time at which the composition (or temperature) at the interface in the liquid reaches the experimentally determined value, and take this time as  $t = 0$ . At this time the composition profile in the liquid will approximate the initial composition profile present during the stabilization of the interface. This approach is valid only if the dynamics are purely diffusive and no liquid droplets or liquid channels are present in the solid near the interface.

When liquid droplets or liquid channels are present in the solid, the rate of the boundary layer build-up is complex since it is governed not only by the diffusion, but also by the rate at which the droplets migrate to the interface and become incorporated into the liquid. For this case we consider the initial composition profile to follow an exponential decay in the liquid and take the initial composition profile in the liquid at  $t = 0$  as:

$$C - C_0 = (C_i - C_0) \exp(-z/\delta),$$

where  $C_i$  is the experimentally determined initial interface composition and  $\delta$  is the initial boundary layer thickness that can be obtained from the experimental slope of the interface composition variation in solid with time at  $t = 0$  when the sample is moved for directional solidification. To determine the value of  $\delta$  for given experimental conditions, we first use the numerical model to obtain a relationship between  $\delta$  and  $(\partial C_i / \partial t)_{t=0}$  for given experimental conditions and then determine the value of  $\delta$  from the experimental measurement of  $(\partial C_i / \partial t)_{t=0}$ . Using the experimentally determined values of  $C_i$  and  $\delta$ , we input the initial composition profile as the boundary condition at  $t = 0$  in the numerical model to calculate the variation in interface position with time and interface temperature with time for the experimental conditions of Figure 1a and b. The



**Figure 4.** A comparison of experimental data (circles) on the variation in (a) interface position and (b) interface temperature with time with the predictions of the theoretical model (solid line) that includes the presence of the initial boundary layer for the experimental conditions of Figure 1.

calculated values, given in Figure 4a and b, show an excellent agreement with the experimental results.

Through detailed experimental studies in a well-characterized alloy system using a thin sample in which convection effects are negligible, the presence of an initial solute boundary layer is observed that needs to be incorporated into models of the initial transient. When our model is modified to include this initial boundary layer, an excellent agreement with the experimental results is obtained.

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Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.scriptamat.2014.10.019>.

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