EFFECT OF THERMAL DRIFT ON THE INITIAL TRANSIENT BEHAVIOR IN DIRECTIONAL SOLIDIFICATION OF A BULK TRANSPARENT MODEL ALLOY

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Abstract

In situ monitoring of directional solidification experiments on a transparent model alloy was carried out under low gravity in the Directional Solidification Insert of the Device for the Study of Critical Liquids and Crystallization (DECLIC-DSI) on-board the International Space Station. The present work is focused on the analysis of the interface recoil and its macroscopic shape evolution. Theoretically the interface movement is due to the formation of a solute boundary layer in front of the interface. However, the bulk configuration and the thermal specificities of transparent systems induce thermal effects, which are usually not observed in the classical thin sample configuration. Numerical thermal modeling highlights two thermal contributions to the interface recoil, both increasing with pulling rate. The Warren and Langer model is modified to take into account these contributions that modify the interface dynamics, and a good agreement is obtained between the experiments and the modified model.

Introduction

In order to design and process new materials, the study of solidification microstructures formation is crucial, as the interface patterns formed by solidification largely govern its mechanical and physical properties. One of the main techniques used to precisely study the fundamental aspects is the directional solidification, where the vertical Bridgman method is one of the most widely used since it has the advantage of steady temperature fields and a controllable temperature gradient.

The wide use of transparent organic analogs that behave like metallic alloys regarding solidification is related to their transparency to visible light, so that *in situ* and real time observation of the interface can be done by classical optical techniques [1, 2]. Many experiments on transparent systems have been conducted in thin samples [3-6], which led to significant progress in understanding the dynamics of solidification. However, these configurations are not representative of three-dimensional (3D) samples and quantitative data extracted from thin samples cannot be extrapolated to 3D configuration. Bulk experiments are therefore required and essential. However, in 3D samples there is a complex coupling between fluid flow and morphological instability: ground-based studies, in both metallic and organic alloys, clearly

showed that the fluid convection on Earth modifies the structure of the solute boundary layer, causing non-uniform morphological instability along the interface [7, 8]. Fluid flow elimination in 3D samples requires the reduced gravity environment of space.
The present study was conducted on board the International Space Station (ISS) in the framework of the French Space Agency (Centre National d'études Spatiales, CNES) project MISOL3D (Microstructures de Solidification 3D) and National Aeronautics and Space Administration (NASA) project DSIP (Dynamical Selection of 3D Interface Patterns). Experiments were realized using the directional solidification insert (DSI) of the Device for the study of Critical Liquids and Crystallization (DECLIC) developed by CNES, which is dedicated to *in situ* and real time characterization of the dynamical selection of the solid-liquid interface morphology on bulk samples of transparent materials [9-11].
A transient period is always present as the first stage of the evolution of the solid-liquid interface from rest to a steady state characterized by a growth velocity equal to the applied pulling rate. Theoretical models assume that, at rest, initially the smooth interface is located on the *liquidus* isotherm, at a fixed position determined by the thermal profile in the adiabatic area. The motion from the initial interface position (*liquidus* isotherm) to its steady state one (*solidus* isotherm in case of planar front growth) is called front recoil, the duration of which also defines the initial transient [12, 13]. One important point to note is that the growth microstructure usually develops during the initial solidification transient. Analyzing the dynamics of this initial transient is thus critical for the understanding of the final steady state microstructure. In this work, experiments will be analyzed in terms of their solidification front recoil.

Experimental procedure

The DECLIC-DSI mainly contains two elements: the Bridgman furnace and the experimental cartridge. Complete description of the device and its inserts may be found elsewhere [10, 11]. The experimental cartridge includes a quartz crucible and a system of volume compensation. The cylindrical crucible has an inner diameter of 10 mm and a length that allows ~10 cm of solidification. In this study, we used a succinonitrile (SCN) – 0.24wt% camphor alloy. In order to fill the crucible, SCN purified by NASA by both distillation and zone melting was used. The alloy was then prepared by adding the solute. All procedures for sample preparation were carefully realized under vacuum to avoid humidity contamination. Once sealed, the cartridge was inserted inside the Bridgman furnace. The thermal gradient G is imposed by regulating hot and cold zones, located above and below the adiabatic area where the interface is positioned. After the thermal regulation, partial melting is performed (a solid seed of ~20mm is always kept to preserve the oriented single crystal) and the sample is then homogenized for at least 24h before performing solidification. Directional solidification is carried out by pulling the crucible into the cold zone at a constant rate for a length of 60 mm. Experiments with pulling rates V_p ranging from 0.5 to 8μm/s and G=12K/cm will be considered in this work.
The crucible is equipped with a flat glass window at the bottom and an immersed lens at the top. The axial observation is the main observation mode and it takes advantage from the complete axial transparency of the cartridge. This observation mode is used to study the pattern dynamics and characteristics. However in this work the results were obtained from the side view observation, which allows imaging the interface motion as well as its macroscopic shape.

Results

The interface recoil was investigated by measuring the motion of the interface in the adiabatic area using the transverse observation. Fig.1(a) shows a step-by-step evolution of the whole experiment starting from rest for 4 µm/s (G=12K/cm) and Fig.1(b) shows the interface position as a function of the solidified length L (namely the pulled length : $L = V_p\, t$, with t: solidification time) for a set of different pulling rates and a fixed thermal gradient.

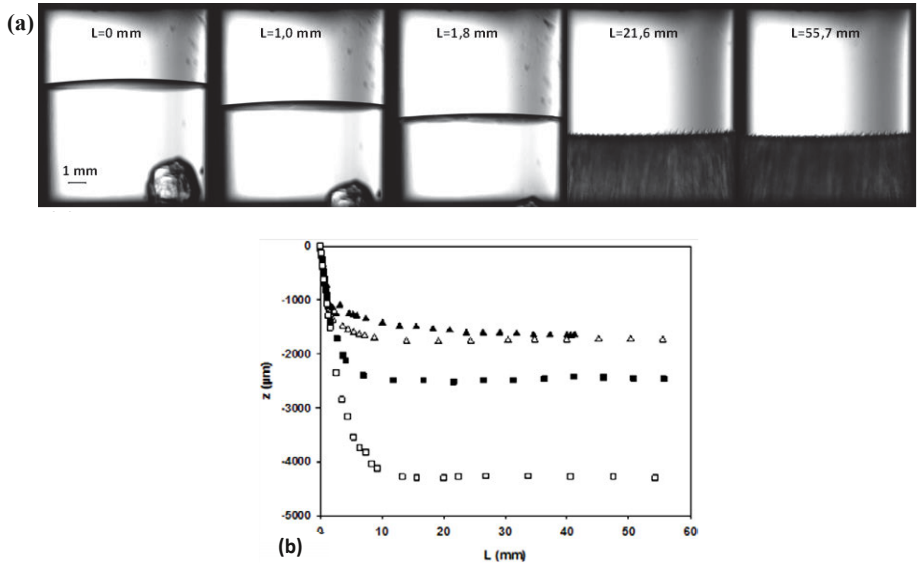

Figure 1 – (a) Interface evolution from rest to steady state under microgravity at G=12K/cm and V_p= 4µm/s; (b) Interface position (z) as a function of solidified length (L) at G=12K/cm for different pulling rates (▲, 1; Δ, 2; ■, 4; □, 8 µm/s).

The build-up of a solute boundary layer ahead of the interface during growth leads to a change of the interface temperature (or interface position) that, for a planar front growth, should reach the *solidus* temperature for the nominal concentration C_0; the recoil associated is named "solutal recoil" with an amplitude of $\frac{m_L C_0}{G}\frac{k-1}{k}$ corresponding to the thermal length l_T (*liquidus* slope m_L=-1.365K/wt%; C_0=0.24wt%; partition coefficient k=0.138 at the *solidus*). For G=12K/cm, this displacement is 1.71mm and is independent of the pulling rate. In all experiments treated, the pulling rate is higher than the critical velocity V_c corresponding to the transition from planar front growth to cellular growth so that a microstructure develops. The cells or dendrites tips grow in the undercooled area towards the liquidus isotherm. Measurements were performed as much as possible at the tips level, as the *solidus* position is unknown. At steady state, tips are located at a distance Δ_t of the *solidus* estimated by the Bower, Brody and Flemings (BBF) expression [14]:

$$\Delta_{t,BBF} = \frac{D_L}{V_p}\left(\frac{V_p}{V_c} - 1\right) = l_T - \frac{D_L}{V_p} \text{ with } V_c = \frac{kGD_L}{(k-1)m_L C_0}$$

where D_L is the solute diffusion coefficient in the liquid (270 µm²/s). Theoretically, the higher the pulling rate, the closer the tips will be from the *liquidus*, and the lower the front recoil will be. However, as can be seen in Fig.1(b), the experimental front recoil increases with pulling rate. This disagreement comes from the theoretical assumption of a frozen thermal field, meaning that the thermal field is neither shifted nor disturbed by pulling. The tip advance as well as the experimental recoil values can be found elsewhere [15].

To analyze the thermal field in the furnace and the interface recoil induced by pulling, the software packages CrysVUn® and CrysMAS® which are designed for the global modeling of solidification processes in complex furnaces with axial or translational symmetry are used. Calculations are based on a method of finite volumes on unstructured grids that enables tackling the entire growth setup on the basis of a geometrical model of the furnace, crucible and sample. It is worth noticing that in these purely thermal simulations, the microstructure is not taken into account: interface recoil therefore corresponds to the motion from the liquidus isotherm to the solidus one, as in a planar front growth. To analyze the different contributions to recoil, additional simulations are performed fixing the latent heat of fusion ΔH to zero. An example of the results for G=12K/cm and V_p=4µm/s is given in Fig.2 (a).

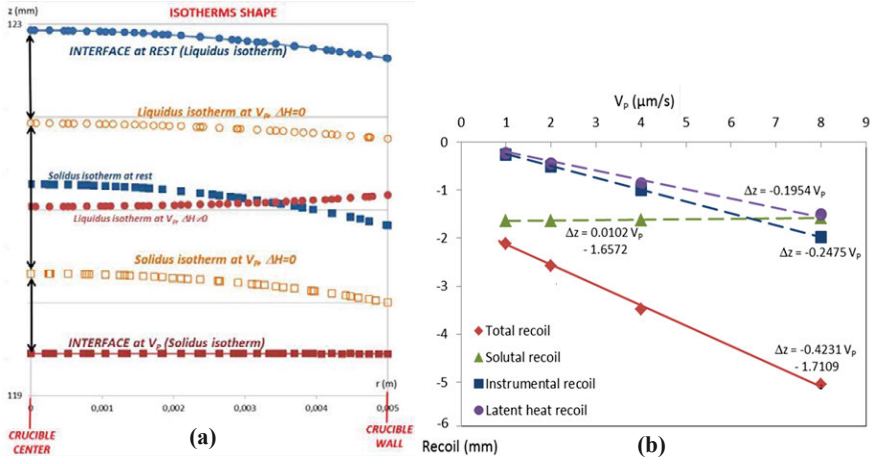

Figure 2 – (a) Position of the *liquidus* and *solidus* isotherms at G=12K/cm. In blue: at rest (V_p=0). In orange: at V_p=4µm/s with a latent heat ΔH=0. In red: at V_p=4µm/s with ΔH ≠ 0; (b) Analysis of the interface recoil with pulling rate (G=12K/cm).

Three different contributions to the recoil are therefore highlighted:

- Instrumental recoil: isotherm shift due to the thermal exchanges induced by pulling deduced from the comparison between *liquidus* isotherm positions at rest and during pulling with ΔH=0;

- Solutal recoil: corresponds to the interface temperature change from the *liquidus* to *solidus* (ΔH=0);
- Latent heat recoil: isotherm shift due to latent heat release measured from the comparison between *solidus* isotherms positions during pulling for ΔH=0 and the normal value of ΔH (3.7kJ/mol).

CrysMAS was then used to determine the sensitivity of the different contributions to recoil to pulling rate (Fig.2(b)). Numerically, the solutal contribution to recoil is roughly insensitive to pulling rate, whereas instrumental and latent heat contributions increase linearly with pulling rate. The total numerical and experimental recoils display the same variation with pulling rate, thus explaining the relative positions of the interface for different pulling rates (Fig.1(b)).

Warren and Langer (WL) [13] developed an approach to describe the acceleration of the interface and the simultaneous build-up of the solutal boundary layer during the initial transient based on the assumption of an exponential transient concentration profile in the liquid, similar to the one obtained in the steady state but with some time-dependent solutal length and solute concentration at the interface. As a result, their model predicts the instantaneous solutal length, interface velocity, solute concentration at the interface and interface position. One assumption behind this model is that the thermal field is frozen so that the recoil is only of solutal origin. We have previously demonstrated that we are not in such a configuration. Thus, the WL model cannot be directly used but it has to be modified to include the thermal effects previously identified. Numerical studies to evaluate the transient interface velocity for purely thermal effects after a velocity jump in a Bridgman furnace [16, 17] concluded that the interface position asymptotically approach its steady state position with a time dependent thermal shift Δz_T [1 - exp(-t/τ)], where t is the time, Δz_T is the total isotherm shift at the steady state resulting from both latent heat release and instrumental recoil, and τ is a delay time dependent of the physical parameters of the alloy, the geometry of the furnace and crucible, the thermal gradient and the pulling rate.

Warren and Langer (WL) [13] formulated the problem in terms of two time-dependent variables: the solute boundary layer thickness l and the interface position z_0 in a reference frame that is moving with a constant velocity V_p, whose origin is taken at the isotherm corresponding to the melting point of the pure solvent (SCN, T_m=58.08°C). A modified WL model was then developed which includes thermal drift by writing the temperature field in a frame translating at velocity V_p in the form:

$$T(z) = T_m + Gz + G\Delta z_T\left(1 - e^{-t/\tau}\right)$$

The interface equilibrium condition is then given by:

$$C_0 = \frac{T_m - T(z_0)}{|m_L|} = -\frac{G}{|m_L|}\left[z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right)\right]$$

where z_0 is the position of the solid-liquid interface in the moving frame and C_0 is the solute concentration on the liquid side of the interface. The dynamical equations of the modified WL model including the thermal drift are the same as the original ones used jointly with the modified interface equilibrium condition:

$$(V_P + \dot{z}_0) = \frac{2D_L}{l}\left[\frac{z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right) - z_\infty}{(1-k)\left(z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right)\right)}\right]$$

$$\dot{l} = \frac{4D_L}{l}\left[\frac{z_\infty - k\left(z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right)\right)}{(1-k)\left(z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right)\right)}\right] - l\left[\frac{\dot{z}_0 + \Delta z_T e^{-t/\tau}/\tau}{z_0 + \Delta z_T\left(1 - e^{-t/\tau}\right) - z_\infty}\right]$$

where l is the instantaneous boundary layer thickness, C_∞ is the fixed nominal concentration of the alloy that is not affected by the thermal drift, z_∞ is the initial position of the interface at rest ($z_\infty = -\frac{|m_L|}{G}C_\infty$), and $\dot{l}$ and $\dot{z}_0$ denote first order time derivatives.

We applied this modified model to analyze our results, treating τ as an adjustable parameter. Δz_T was used as input into the model for each pulling rate and it was deduced from experiments taking into account the theoretical solutal recoil and the tip advance. The best fit results are presented in Fig.3. The predictions result from a least squares fit with τ against the experimental data at early time (L≤2mm) while the solid-liquid interface is still planar before morphological destabilization.

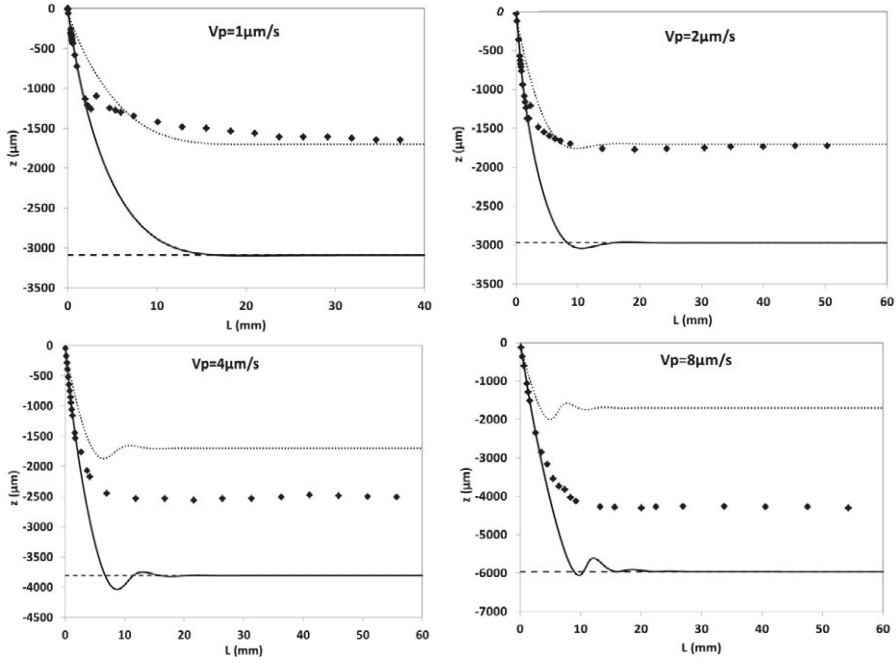

Figure 3 – Interface position ($z = z_0 - z_\infty$) as a function of solidified length (L) for different pulling rates: experimental points are superimposed with the modeling results using Warren and Langer [13] model modified to take into account the isotherm shift (full line) and the original model (dotted line), for G=12K/cm. The dashed line corresponds to the estimated *solidus* line.

The results presented in Fig.3 illustrate the good agreement obtained between the experimental and modeling results during early microstructure development (initial transient). The dashed line

corresponds to the estimated *solidus* position using BBF model and it can be seen that the model results converge to this value once the steady-state is attained. The fitted values of τ, as well as the values of Δz_T, are presented in Table 1. It can be seen that τ decreases with V_p. The dotted line in Fig.3 corresponding to the predictions of the original WL model (i.e. Δz_T=0) highlights the importance of the thermal drift contribution to accurately reproduce the experimental measurements. Additional results can be found elsewhere [15].

Table 1 – Δz_T values and fitted values of the delay time τ(s) used in the modified WL model considering a BBF tip undercooling for G=12K/cm.

V_p (μm/s)	Δz_T (mm)	τ(s)
1	1.39	1998
2	1.60	837
4	2.44	563
8	4.26	487

Conclusion

This work was realized in the framework of the DECLIC-DSI project, dedicated to *in situ* and real time observation of the solid-liquid interface during directional solidification of bulk transparent alloys. DECLIC was installed on board the ISS, under microgravity, thus avoiding fluid flow influence. Even if the main observation mode of this device is the axial observation, the data presented here come from the side view observation, which enables the study of the interface motion during the whole experiment. The experiments analyzed have been carried out on a transparent organic alloy (succinonitrile-0.24wt% camphor).

Thermal analyses were performed revealing two contributions to interface motion during pulling. These contributions add to the standard physical recoil that corresponds to the interface temperature change from the *liquidus* to the *solidus*. These contributions justify the qualification of a not frozen thermal field, and they increase linearly with pulling rate.

Experimentally, the evolution of the interface position as a function of the solidification length was measured for different pulling rates. The global interface recoil increase with pulling rate is compatible with a not frozen thermal field condition. The WL model was modified to take into account the isotherm shift contribution and a good agreement was obtained between experiments and the modified model.

The present work gave a better understanding of the general front behavior for geometrical configurations not associated to a frozen thermal field, and it clearly appeared that the thermal transients have to be taken into account for a complete understanding of front dynamics for such bulk samples.

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