

Solute Trapping in Highly Undercooled Succinonitrile-Acetone Alloys

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Abstract

Pure succinonitrile and three dilute succinonitrile-acetone alloys were undercooled in long and fine capillary tubes up to the hypercooling limit. Solidification was externally triggered and growth into the undercooled melt optically monitored. The undercooling dependence of the growth velocity was measured systematically for the pure material and the three alloys. It was found that above $\Delta T = 10$ K all V - ΔT curves were parallel. Motivated by this observation it is shown that with freely growing alloy dendrites the only mechanism for parallel V - ΔT curves is complete solute trapping. From the parallel shift of the curves the T_0 -temperature can be estimated. Although in the presented experiments thin surface dendrites grow along the tube wall, and therefore the results for free growing dendrites cannot be adapted directly, the agreement between the theoretically estimated T_0 -temperatures and the temperatures estimated from the measurements is remarkable. From this observation and three additional assumptions it is proposed that in the succinonitrile-acetone system complete solute trapping occurs above a growth velocity of $V = 0.4$ m/s.

Introduction

In the vast majority of solidification processes, the advance of the solid/liquid interface is slow enough for thermodynamic equilibrium at the solidification front to be a reasonable approximation [1]. Usually the solubility of solute in solid and liquid in equilibrium is different and solute partitioning leads to segregation phenomena. However, if the solid/liquid interface advances rapidly, partitioning can not follow and solute trapping occurs [1, 2, 3]. Thus the solute content of the solid growing from the melt is higher than that predicted from the phase diagram. In the extreme case of very rapid solidification there is no partitioning whatsoever and a solid forms with the same concentration as the liquid. This is called complete solute trapping.

Recently complete solute trapping was found in metallic samples solidified from highly undercooled melts [4, 5]. Solute trapping in organic model material such as succinonitrile-acetone (SCN-ACE) has never been reported. In this paper we report undercooling experiments with highly undercooled SCN-ACE alloy melts. Based on systematical growth rate measurements we will present evidence that complete solute trapping does occur in this organic system.

Experimental procedure

The transparent organic metal-like solidifying material SCN was first purified by zone-melting to a degree better than 99.995% and then alloyed with acetone. Borosilicate quartz tubes, 0.9 m in length, with a square cross section of $400 \times 400 \mu\text{m}^2$ and an inner edge length of $200 \mu\text{m}$, were filled with pure SCN and three different dilute alloys of SCN-ACE. After hermetically sealing the samples a segment of 0.1 m length was placed into a water jacket. This water jacket was held at

constant temperature by using a high precision thermostat. By means of a self-constructed micro heating the two seals where the capillary tube enters the water jacket were kept at a temperature higher than the melting point. Undercooling was achieved by lowering the temperature of the water jacket from above the melting point to the desired undercooling temperature while keeping the melt inside the seals permanently above melting point. After having reached thermal steady state, solidification was initiated by lowering the temperature at one entrance seal and thus allowing the solid outside the water jacket to grow into the undercooled melt. At a position where steady state growth was established, the growth rate was measured. For that purpose the change in light transmission due to the appearance of curved solid/liquid interfaces was registered with two independent photo diodes. From the distance between the photo diodes and the time difference between the monitored signals the growth velocity, V , was estimated. Fig. 1 shows the experimental set-up. Further experimental details are given in [6, 7].

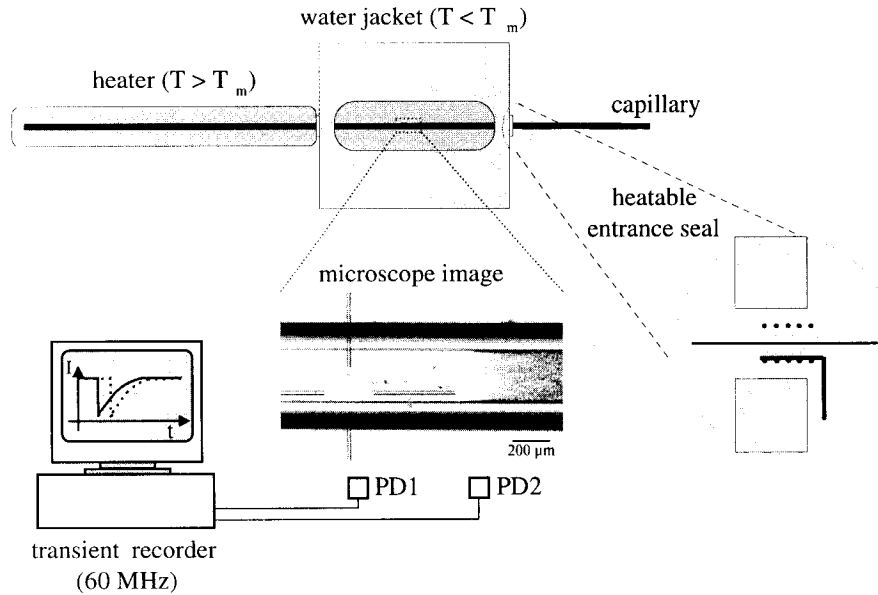


FIG. 1 Experimental set-up used for measuring the growth velocity in undercooled SCN-ACE alloy melts. Growth was initiated by reducing the temperature inside an entrance seal, thus allowing the solid outside the water jacket to spread into the undercooled segment. The growth velocity was measured by registering the change in light transmission at two positions with photodiodes (PD).

Results

Optical investigations of the solidification process for $\Delta T < 5$ K showed that the solid first grows as thin "surface dendrites" along the capillary tube walls before spreading into the tube interior. There is evidence that this statement is also true for larger undercoolings [7]. Thus, the measured growth rates do not represent the velocity of free growing dendrites. The exact geometrical shape of the solid layer growing along the tube wall (especially for large undercoolings) was not determinable.

With the technique described above the relation between the growth rate V and the undercooling ΔT was measured for pure SCN ($\Delta T = T_f - T_\infty$, T_f : melting point, T_∞ : temperature of the undercooled melt) and the three dilute SCN-ACE alloys ($\Delta T = T_L - T_\infty$, T_L : liquidus temperature) from $\Delta T = 0.1$ K up to the hypercooling limit $\Delta T_{\text{hyp}} = 23.14$ K. Within this undercooling range the growth rate was

found to change by about five orders of magnitude. Fig. 2 shows the measured V - ΔT relations in a log-log plot (Fig. 2a) and a lin-lin plot (Fig. 2b). Fig. 2a shows that for larger ΔT the V - ΔT curves of the SCN-ACE alloys approach the curve of the pure SCN. Thus the influence of the alloying element decreases with increasing undercooling. For $\Delta T > 10$ K all four measured V - ΔT curves were found to be parallel (Fig. 2b).

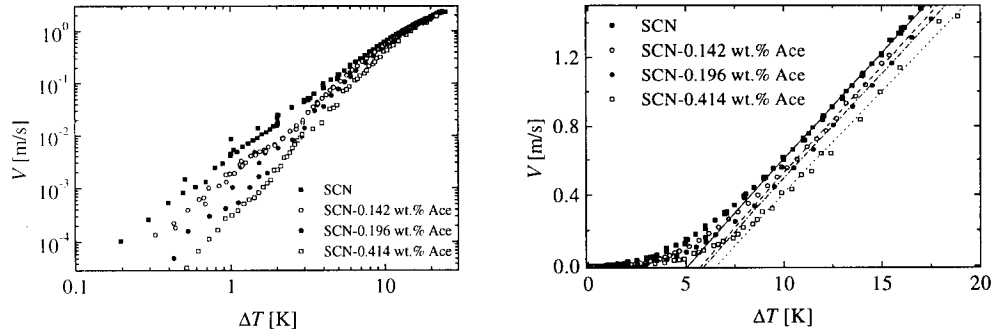


FIG. 2 Growth velocity as a function of undercooling for pure SCN and the three dilute SCN-ACE alloys in a log-log plot (left) and in a lin-lin plot (right). The measured curves are parallel above an undercooling of $\Delta T = 10$ K.

Discussion

Although the solid did not grow as a free dendrite into the undercooled melt it is important to recall the dendritic growth theory to interpret the observations. For an alloy dendrite growing into an undercooled melt, Lipton et al. [8] used the marginal stability criterion as the working point for the dendrite tip radius R . According to [9] this criterion can be expressed as

$$R = \sqrt{\frac{\Gamma/\sigma^*}{mG_C\xi_C + G_T\xi_T}} \quad (1)$$

where Γ is the Gibbs-Thomson coefficient, $\sigma^* = (4\pi)^{-1}$ the stability constant, m the liquidus slope and G_C and G_T are solutal and thermal gradients. The stability functions, ξ_C and ξ_T , defined in [9], are functions of the corresponding Péclet number¹⁾ and vary from one for $P_C \ll 1$ and $P_T \ll 1$ to zero for $P_C \gg 1$ and $P_T \gg 1$, respectively. Eq. (1) shows that a transition from solutal to thermal growth occurs with increasing V [8]. This transition appears when the solute absolute stability limit is reached, $V \approx (V_a)_C := \Delta T_0 D / (k_V \Gamma)^2$. For $V \gg (V_a)_C$ the growth is governed by the thermal diffusion field alone (pure thermal growth) and Eq. (1) changes accordingly into

$$R^2 V = \frac{2a \cdot \Gamma / \sigma^*}{(\Delta h_f / c_p) \cdot \xi_T} \quad (2)$$

¹⁾ $P_C := VR/(2D)$ and $P_T := VR/(2a)$ with diffusion coefficient D of solute in the melt and thermal diffusivity a .

²⁾ ΔT_0 is the liquidus-solidus interval and $k_V = (V/V_D + k)/(V/V_D + 1)$ the non-equilibrium distribution coefficient [2], with the diffusion velocity across the interface V_D which is often taken as $V_D = D/\delta$ (δ : interface thickness).

where Δh_f is the latent heat of fusion and c_P the heat capacity. In other words, for $V \gg (V_a)_C$ alloy dendrites do grow with the same radius as the corresponding pure dendrites.

According to [8] the bath undercooling ΔT can be divided into thermal undercooling ΔT_T , curvature undercooling ΔT_R , kinetic undercooling³⁾ ΔT_k , constitutional undercooling ΔT_C , and change of the "liquidus temperature" due to solute trapping³⁾ ΔT_L :

$$\begin{aligned} \Delta T &= \Delta T_T + \Delta T_R + \Delta T_k + \Delta T_C + \Delta T_L \\ &= \Delta T_{hyp} \text{Iv}(P_T) + \frac{2\Gamma}{R} + \frac{V}{\mu} + m_v C_0 \left[1 - \frac{1}{1 - (1 - k_v) \text{Iv}(P_C)} \right] + (m - m_v) C_0 \end{aligned} \quad (3)$$

where $m_v := m \cdot (1 - k_v + k_v \ln(k_v / k)) / (1 - k)$ is called the "velocity dependent liquidus slope".

Comparing a pure and an alloy dendrite both growing with equal $V \gg (V_a)_C$ (and according to the above statement with equal R and thus with equal P_C and P_T), from Eq. (3) the conclusion can be drawn that ΔT_T , ΔT_R and ΔT_k are equal for both dendrites. Consequently, differences in the bath undercooling ΔT_{dif} necessary to obtain the same V can only be due to the terms ΔT_C and ΔT_L (which are of course zero for the pure dendrite). For $V \gg (V_a)_C$ the constitutional undercooling term simplifies to $\Delta T_C = m_v C_0 (1 - 1/k_v)$. This is the V -dependent liquidus-solidus range.

Considering the case that for $V \gg (V_a)_C$ $\Delta T_{dif} = \Delta T_C + \Delta T_L$ is independent of V – i.e. the V - ΔT curves of the pure and alloyed material are parallel for $V \gg (V_a)_C$ – the term m_v / k_v must be independent of V . This can only be achieved by $k_v \approx 1$, i.e. for complete solute trapping. For the differences in bath undercooling it follows

$$\Delta T_{dif} = m C_0 \cdot \left(1 - \frac{\ln(k)}{(k - 1)} \right). \quad (4)$$

The temperature at which the free energies of a solid and a liquid both with the same concentration are equal, is the T_0 -temperature. For dilute binary alloys Boettinger and Corriell derived the following expression for T_0 [3]

$$T_0 = T_f + m C_0 \cdot \frac{\ln(k)}{(k - 1)}. \quad (5)$$

Inserting Eq. (5) into Eq. (4) and using the simple expression $T_L = T_f + m C_0$ results in

$$\Delta T_{dif} = T_L - T_0. \quad (6)$$

Consequently it can be concluded that a dilute alloy which solidifies with complete solute trapping into an undercooled melt behaves like the pure solvent with the hypothetical "melting point" of T_0 .

³⁾ This contribution to the total bath undercooling is not explicitly used in [8] but should be considered due to [1, 8].

In conclusion the presented analysis shows that in cases where the V - ΔT curves of the pure and alloyed material are parallel for $V \gg (V_a)_C$, the T_0 -temperature can be determined from the shift of these curves. This statement has been derived for dilute binary alloys. However, it seems unlikely that for non-dilute alloys the V -independence of $\Delta T_C + \Delta T_L$ can be achieved without considering $k_V \approx 1$.

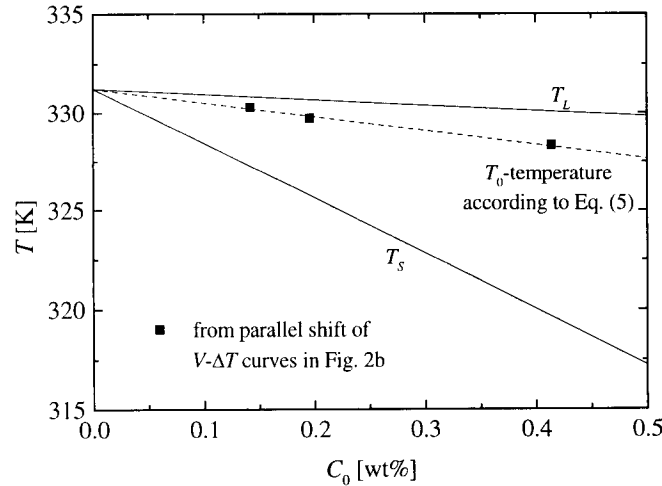


FIG. 3 SCN-ACE phase diagram with the T_0 temperature calculated from Eq. (5). The experimental points are estimated by reducing T_L by the corresponding parallel shift of the V - ΔT curves shown in Fig. 2.

Although the above argumentation is valid only for free growing dendrites, we have applied Eq. (6) to the parallel curves shown in Fig. 2b. Fig. 3 shows the resulting temperatures together with the T_0 -temperature calculated with Eq. (5). The agreement is remarkable. However, for the surface dendrites a growth theory similar to the one used above is not available. Thus, further considerations are needed to draw conclusions from Fig. 3. The reason for the lack of a theory is that the tip geometry of a surface dendrite is not known exactly and that the thermal and the solute diffusion fields around the tip is unsymmetrical due to the influence of the tube wall. In addition, it is not known whether or not Young's triple-point-law is valid for the rapidly moving triple point glass/solid/liquid.

Although with the surface dendrites the analytical expressions for ΔT_T and ΔT_C are not known it is obvious that the bath undercooling can still be divided as $\Delta T = \Delta T_T + \Delta T_R + \Delta T_k + \Delta T_C + \Delta T_L$. The expression for ΔT_k and ΔT_L are similar for free growing dendrites and for surface dendrites. For the interpretation of the result shown in Fig. 3 we make the following three assumptions on surface dendrites:

- (i) A defined geometrical dimension R_S (similar to the tip radius in free growth) governs the growth at the tip region of a surface dendrite;
- (ii) ΔT_R and ΔT_T are functions of V and/or R_S ;
- (iii) For $V \gg (V_a)_C$ the growth is governed by the thermal field alone (pure thermal growth). Thus, it can be concluded that even for surface dendrites ΔT_C is given by the V -dependent liquidus-solidus range.

In our experiments the condition $V \gg (V_a)_C$ is fulfilled for at least the highest velocity measured. The solute absolute stability limits for the three investigated alloys calculated with the equilibrium distribution coefficient are $(V_a)_C = 0.7$ m/s, 1 m/s and 2.1 m/s, and with $k_V \approx 1$ $(V_a)_C = 0.07$ m/s, 0.1 m/s and 0.21 m/s, respectively.

With the made assumptions it follows that for $V \gg (V_a)_C$ $\Delta T_{diff} = \Delta T_C + \Delta T_L$ holds even for surface dendrites. Thus, parallel V - ΔT curves as shown in Fig. 2b leads to the necessity that the term m_V/k_V is independent of V , from which $k_V \approx 1$ directly follows. Therefore, we conclude that if the above assumptions are valid, in the system SCN-ACE complete solute trapping occurs for $V > 0.4$ m/s. This conclusion is remarkable. From the common estimation of $V_D = D/\delta$ it is assumed that complete solute trapping should be present for $V \gg V_D \approx 1$ m/s. On the other hand, diffusivity across the solid/liquid interface is not well approximated by the diffusivity of solute in the pure liquid. In fact, the only reliable statement on the diffusivity across the interface is that it must be lower than liquid diffusivity and higher than solid diffusivity.

Conclusions

In summary the following conclusions can be drawn from this work:

- If for freely growing dendrites the V - ΔT curves of a pure and an alloyed material are parallel, it can be concluded that complete solute trapping must be present.
- Although surface dendrites are present in our experiments it is found that the agreement between the theoretically estimated T_0 temperature and the temperature estimated by reducing T_L by the corresponding parallel shift of the measured V - ΔT curves is remarkable.
- From this observation and due to three reasonable assumptions on surface dendrites it is proposed that in the SCN-ACE system complete solute trapping occurs above a growth velocity of $V = 0.4$ m/s.

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