Dendritic growth velocity and diffusive speed in solidification of undercooled dilute Ni-Zr melts

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Abstract

During rapid solidification of undercooled melts deviations from local equilibrium occur at the solid–liquid interface. With increasing interface velocity \( v \), the interfacial undercooling \( \Delta T \) increases and solute trapping becomes important. These phenomena are well characterized for planar interfaces, but for dendritic growth they must be incorporated into dendrite growth theory and the combination tested. The predictions of dendrite growth theory are very sensitive to the diffusive speed—the interface speed at which the solute trapping function is in mid transition between local equilibrium and complete trapping. Dendrite growth velocities have been measured as a function of undercooling in levitated droplets of \( \text{Ni}_{52}\text{Zr}_{48} \) alloys. The results are described within current theory of dendrite growth taking into account deviations from local equilibrium. The diffusive speed is independently determined by preliminary pulsed laser melting experiments on thin film specimens for the same alloy system. Best fit values of the diffusive speed inferred from both sets of measurements are similar in magnitude. Given the preliminary nature of the pulsed laser melting measurements, this result is encouraging for the prospects of a parameter-free test of modern dendrite growth theory. © 1997 Elsevier Science S.A.

Keywords: Rapid solidification; Dendrite growth; Solute trapping

1. Introduction

Undercooling of a melt gives rise to a driving force for crystallization due to the difference between the Gibbs free energy of the undercooled liquid phase and that of the solid phase. For deeply undercooled melts, the driving force for resolidification becomes large enough to move the system into the regime of rapid solidification where assumptions of local equilibrium break down. This deviation from local equilibrium manifests itself as a local undercooling of the interface and as a deviation from the chemical equilibrium at the solid–liquid interface. Modern dendrite growth models [1,2] take into account such non-equilibrium effects by introducing a kinetic undercooling of the solid–liquid interface and a dependence of the partition coefficient on the growth velocity. The latter effect is described by the solute-trapping model of Aziz [3]. In the dilute concentration limit of alloys the velocity dependence of the partition coefficient \( k = k(v) \) is expressed by:

\[
k = \frac{k_{\infty} + v/v_{D}}{1 + v/v_{D}},
\]

where \( k_{\infty} \) is the equilibrium partition coefficient, \( v \) is the interface velocity and \( v_{D} \), the diffusive speed, is treated as a free parameter. Laser resolidification experiments on thin films in combination with the determination of concentration profiles in the as-solidified samples by Rutherford backscattering spectroscopy (RBS) enable the measurement of \( k(v) \) and therefore a determination of \( v_{D} \) as well. Such experiments on a variety of different dilute alloys have confirmed the validity of Eq. (1) for planar growth in thin films [4–7].

In the case of undercooled melts we have to deal with free dendritic growth. At large undercoolings, the driving force can cause dendrite growth velocities in the range of 1–100 m s\(^{-1}\) [8,9] which are comparable with rapid crystal growth in laser resolidification experiments. The analysis of dendrite growth theory assumes the validity of Eq. (1) even though there is not a planar interface. In the present work both the dendrite growth velocity is measured as a function of undercooling and the diffusive speed in laser heat melted thin films on the same sample system of dilute Ni-Zr alloys. The combination of these results may be used to describe rapid dendrite growth without any adjustable parameter.
2. Experimental details

Electromagnetic levitation is used for containerless undercooling of bulk drops [10]. The experiments are conducted in a UHV chamber which was evacuated to a pressure of $10^{-7}$ mbar and backfilled with a purified He-$\text{H}_2$ gas mixture (20 vol.% $\text{H}_2$). The avoidance of container-wall induced nucleation and highly pure environmental conditions leads to reproducible maximum undercoolings of $\Delta T = 300 \text{ K}$ prior to nucleation. The freely suspended drops are accessible to direct observations of rapid solidification and the temperature of the sample is measured at its top by a two-color pyrometer with an accuracy of $\pm 5 \text{ K}$. Crystallization of the undercooled melt is stimulated at its lower end by using an Alumina stimulii needle. The solidification starts at this well defined point and the array of dendrites grows radially into the melt. A rapid photosensing technique is utilized to measure the velocity of the advancing solidification front as a function of undercooling [11]. The pyrometrically detected temperatures of a small square area of the sample surface were read into a transient recorder at a sampling rate of up to 1 MHz. The temperature, $\Delta t$, needed by the envelope of the dendrite tips to sweep across the sensitive area of the photodiode of the width $\Delta s$ is measured, and the dendrite growth velocity is given by $v = \Delta s/\Delta t$. The results of these velocity-undercooling measurements are analyzed within current dendrite growth models [1,2].

The diffusive speed is independently measured by a pulsed-laser resolidification technique described elsewhere [4–7]. A thin film ($\sim 2700 \text{ Å}$) of Ni was deposited by electron beam evaporation on an Si wafer covered with 2000 Å of thermally grown SiO$_2$. Ion implantation of $^{90}\text{Zr}^+$ was used to place the peak in solute concentration at 300 Å beneath the free surface. The wafers were then patterned and etched for transient reflectance and transient conductance measurements of interface positions and velocities. Laser melting was performed with a single 35 ns excimer laser pulse (KrF: 248 nm) at fluences of 0.4–0.7 J cm$^{-2}$ to yield a solidification velocity of 2.8 m s$^{-1}$. Initial and final concentration profiles of Zr were obtained using RBS grazing-angle techniques [7] which produce a depth resolution of 60 Å. The analysis of the diffusive speed was performed by comparing the measured final concentration profile to one predicted by computer simulation. The simulation utilized a Crank–Nicholson algorithm to solve the 1-dimensional diffusion equation for the molten portion of the sample. The values of the liquid diffusivity and the diffusive speed are then determined by a best fit between the experimental and simulated curves.

Dilute Ni$_{90}$Zr$_{10}$ alloys were chosen for the present experiments because of several considerations. They are undercoolable by electromagnetic levitation experiments. Another favorable property of the Ni-Zr system at small Zr amounts is its small equilibrium partition coefficient $k_e$ on the order of $10^{-3}$. Therefore, a strong solute trapping effect is expected at growth velocities which are observable both in the undercooling experiment as well as in the laser resolidification experiments. An additional requirement for the measurements of the partition coefficient by RBS is that the solute (Zr) be significantly heavier than the solvent in order to resolve the solute depth profile. For the electromagnetic levitation experiment, alloys of Ni$_{90}$Zr$_{10}$ were prepared from constituents of Ni and Zr both of a purity better than 99.99%. They were melted in situ under a high purity He gas atmosphere in a radio frequency levitation coil into spheres of about 6 mm diameter. The mass of the sample amounts to about 1 g. For the laser resolidification experiment, the Ni used for evaporation was 99.99% and the Zr was implanted to give a peak concentration of 0.5–1 atomic percent.

3. Experimental results and discussion

3.1. Measurement of dendrite growth velocities

Fig. 1 shows the experimental results for the measurements of the dendrite growth velocity as a function of undercooling on dilute Ni$_{90}$Zr$_{10}$ alloy (cf. dots in Fig. 1). At small undercooling the growth velocity is rather sluggish. If the undercooling approaches a critical undercooling of $\Delta T_{cr} \approx 190 \text{ K}$ a steep rise of the growth velocity with increasing undercooling is observed. Such a behaviour in the velocity versus undercooling relation has previously found in dilute Ni-B alloys [9].

![Graph showing dendrite growth velocity vs. undercooling](image-url)

Fig. 1. Dendrite growth velocity $v$ as a function of undercooling $\Delta T$ for Ni$_{90}$Zr$_{10}$. Experimental results are represented by the dots. The solid line gives the prediction of dendrite growth theory taking into account a velocity dependent partition coefficient. For comparison, the dotted line gives the results of computations within dendrite growth theory but neglecting solute trapping. A satisfactory description of the experimental results can only be achieved if a velocity dependent partition coefficient is taken into consideration.
Table 1
Material parameters used for the calculation of the dendrite growth velocities as a function of undercooling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of fusion</td>
<td>$\Delta H$ [J mol$^{-1}$]</td>
</tr>
<tr>
<td>Specific heat of the liquid</td>
<td>$c_p$ [J mol$^{-1}$ K$^{-1}$]</td>
</tr>
<tr>
<td>Thermal diffusivity</td>
<td>$D_T$ [m$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D_L$ [m$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>Equilibrium partition coefficient</td>
<td>$k_e$</td>
</tr>
<tr>
<td>Diffusive speed</td>
<td>$v_D$ [m s$^{-1}$]</td>
</tr>
<tr>
<td>Liquidus slope</td>
<td>$m$ [K at.%]</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>$v_0$ [m s$^{-1}$]</td>
</tr>
</tbody>
</table>

For an analysis of the experimental results we apply current theories of dendrite growth [1,2]. Correspondingly, the total undercooling $\Delta T$ is expressed as the sum of four different terms:

$$\Delta T = \Delta T_i + \Delta T_c + \Delta T_T + \Delta T_k,$$  \hspace{1cm} (2)

with the individual contributions of the thermal undercooling $\Delta T_i$, the constitutional undercooling $\Delta T_c$, the curvature undercooling $\Delta T_T$ and the kinetic (interface friction) undercooling $\Delta T_k$. These are expressed as

$$\Delta T_i = \frac{\Delta H_i}{c_p} F_i (P_i)$$ \hspace{1cm} (2a)

$$\Delta T_c = m c_0 \left( 1 - \frac{m^v/m}{1 - (1 - k(v) F_i (P_c))} \right)$$ \hspace{1cm} (2b)

$$\Delta T_T = \frac{2 \Gamma}{R}$$ \hspace{1cm} (2c)

$$\Delta T_k = \frac{v}{\mu}$$ \hspace{1cm} (2d)

Here, $F_i (x) \equiv x \exp (x) E_1 (x)$ denotes the Ivantsov function (with $E_1$ the first exponential integral function), $P_i = v R / 2 D_T$ the thermal Péclet number (with $v$ the interface velocity, $R$ the curvature radius of the dendrite tip), $m^v$ the velocity dependent liquidus slope, $c_0$ the nominal concentration of the alloy, $P_e = v R / 2 D_L$ the chemical Péclet number, $\Gamma = s / D_S T_L$ the Gibbs–Thomson coefficient (with $s$ the solid–liquid interface energy, $\Delta S_f$ the entropy of fusion), $\mu = (\Delta H (v_0)) / (k_b T_L^2)$ the interfacial kinetic coefficient according to the model of collision limited growth [12] (with $k_b$ the Boltzmann constant) and $T_L$ the liquidus temperature. The other symbols are explained in Table 1.

Eq. (2) describes the undercooling in terms of the product of the growth velocity $v$ times the dendrite tip radius $R$. For a unique calculation of the dendrite growth velocity as a function of undercooling we use the criterion of marginal stability [13] which gives an expression of the dendrite tip radius:

$$R = 4 \pi^2 \Gamma \left[ \frac{\Delta H_i}{c_p} F_i (P_i) \frac{2 \cdot m \cdot c_0 (1 - k(v) F_i (P_c))}{1 - (1 - k(v) F_i (P_c))} \right]^{-1}$$ \hspace{1cm} (3)

where

$$\xi_1 = 1 - (1 + (2 \pi / P_j)^2)^{-1/2}$$ \hspace{1cm} (3a)

and

$$\xi_c = 1 - \frac{2 \kappa}{2 \kappa - 1 + (1 + (2 \pi / P_j)^2)^{1/2}}$$ \hspace{1cm} (3b)

The solid line in Fig. 1 represents the results of the calculations according to Eq. (2) and Eq. (3) if the material parameters are used for the computations as listed in Table 1. In the undercooling range of $\Delta T \lesssim 220$ K the measured data are well described by theory. In particular, the steep rise of the growth velocity in the vicinity of the critical undercooling $\Delta T_{cr}$ is predicted by theory in a correct way. For comparison, the dotted line in Fig. 1 shows the equivalent result of the growth velocity calculation with the solute trapping effect neglected. The measured data can only be reproduced by the theory if a velocity dependent partition coefficient is used to calculate the constitutional undercooling $\Delta T_c$. Hence, solute trapping has a pronounced influence on the $v - \Delta T$ relation.

For a further analysis of solute trapping during rapid dendrite growth the concentrations at the dendrite tip in the liquid $c_L$ is calculated according to

$$c_L = \frac{c_0}{1 - (1 - k(v) \cdot F_i (P_c))}$$ \hspace{1cm} (4)

The concentration in the solid $c_s$ is then found by applying the definition of the partition coefficient, $c_s = k \cdot c_L$. The results of these computations are plotted as a function of the undercooling in Fig. 2. At small undercoolings the Zr concentration in the liquid rises due to the rejection of the solute atoms (limited solubility) and

![Graph](image-url)
the concentration profiles follow the equilibrium values (cf. solid lines in Fig. 2). This means there is strong partitioning in front of the slowly advancing interface. If the undercooling is increased into the regime $\Delta T > 90$ K deviations occur which progressively rise with undercooling. At large undercoolings $\Delta T > \Delta T_{cr} = 190$ K, the liquid approaches the nominal concentration $c_0$ of the alloy. This means at such undercoolings we have reached a regime of complete solute trapping.

With these results in mind the behaviour of the velocity–undercooling relation is understood. At small undercoolings the interface movement is sluggish and controlled by the redistribution of solute in front of the interface. If solute trapping becomes important, the concentration gradient becomes weaker until it diminishes at undercoolings in the vicinity or above $\Delta T_{cr}$. In this undercooling range the constitutional undercooling looses its influence and the growth velocity is only controlled by the thermal gradient in front of the solid–liquid interface. The chemical diffusion coefficient is smaller by three orders of magnitude than the thermal diffusivity. As a consequence, the growth velocity steeply rises in the transition regime around $\Delta T_{cr}$.

### 3.2. Preliminary measurement of the diffusive speed

Fig. 3 shows the comparison of the simulated Zr concentration profile to the experimentally measured solute concentration profile. For this simulation, the maximum melt depth was 1800 Å and the resolidification velocity was 2.8 m s$^{-1}$. The initial concentration profile is allowed to evolve while in the liquid phase according to the diffusion equation using a liquid diffusivity of $0.65 \times 10^{-9}$ m$^2$ s$^{-1}$. This causes a depression of the main peak in the profile as Zr moves to regions of lower concentration. As the sample resolidifies, the interface moves toward the surface causing rejected Zr to pile up in front of the moving interface; eventually the interface reaches the free surface of the film where it deposits the accumulated Zr. This effect creates by the characteristic peak in the concentration profile at the surface in both the simulated and the experimental curves.

The numerical values of $v_D = 28$ m s$^{-1}$ and $D_L = 0.65 \times 10^{-9}$ m$^2$ s$^{-1}$ obtained by the laser resolidification method are comparable to $v_D = 20$ m s$^{-1}$ and $D_L = 2.0 \times 10^{-9}$ m$^2$ s$^{-1}$ as used for the calculation of the dendrite growth velocity in the undercooling experiment. It should be noted that the results from laser resolidification are still in a preliminary stage. The differences between the simulated concentration profile and the final concentration profile in the region 250–750 Å suggest that our results could be prone to certain experimental pathologies. For example, there exists the possibility for interfacial breakdown during resolidification as well as surface gettering of the segregated Zr. Surface gettering would place an artificial high amount of Zr in the surface peak and therefore cause an overestimate of $v_D$. Interfacial breakdown could also result in an artificially high amount of Zr left in deeper regions of the sample and would make our liquid diffusivity appear low. Further investigation must be done before a final result may be obtained. However, given the uncertainties in the laser results at present, the proximity of the combined results should be considered encouraging for the success of dendrite growth theory.

### 4. Conclusion

In the present work we have measured the dendrite growth velocities as a function of undercooling using electromagnetic levitation to obtain containerless undercooling in bulk Ni$_{59}$Zr$_{41}$ alloys. In addition, we have independently obtained the diffusive speed by laser resolidification experiments on thin films of the same alloy for a single growth velocity. The results from laser resolidification are still preliminary. However, they suggest that a fit of the dendrite growth theory without any adjustable parameters is possible.

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References