

Evidence of Nonequilibrium Processes in Rapid Solidification of Undercooled Metals

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Containerless undercooling in an electromagnetic levitation device was used to observe solidification velocities as a function of undercooling temperature for pure Ni and Cu-Ni alloys. In a limited temperature range, the results can be interpreted using current theories, provided the conditions for local equilibrium at the solid-liquid interface are relaxed. Beyond a certain undercooling value, the observations differ markedly from current predictions.

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Rapid solidification processing¹ is a well established method for the preparation of metals in metastable states, giving access to a range of novel materials properties. An important crystal-growth mechanism in these techniques is dendritic growth, which provides the most effective means of heat and solute rejection during solidification. Dendritic growth has attracted recent attention both from the theoretical²⁻⁵ and the experimental side.⁶⁻⁹

Theoretical models of dendritic growth rely on equilibrium thermodynamics and assume a local equilibrium at the solid-liquid interface. For low growth velocities these assumptions have been verified experimentally.⁶ In rapid solidification, analysis of the solidified products points to the possibility of a breakdown of the local equilibrium at the interface.¹⁰ As these conclusions are derived post mortem, after considerable modification of the material through aging processes, it is desirable to obtain direct evidence during the primary solidification stage, which turns out to be exceedingly difficult in techniques relying on rapid heat extraction, such as melt spinning, splat cooling, or atomization.

An alternative way to achieve high solidification velocities is to prevent nucleation in a bulk melt and thus undercool it by a substantial amount. The high driving force for crystallization accumulated in this way leads to a rapid solidification process which can be observed quantitatively.

The present paper reports on direct measurements of the solidification velocity in metals undercooled using an electromagnetic levitation technique. Solidification was initiated actively at a chosen undercooling temperature and in a well defined geometry. The observed dendritic growth velocities show deviations from the predicted behavior, which can be related to a relaxation of local interface equilibrium. For even larger growth rates, a drastic change of the velocity dependence on undercooling is found. This occurs at a growth velocity where the morphology of the solidified product changes from coarse to fine grained.

Measurements were performed on pure nickel metal or

Cu-Ni alloys. Samples were prepared from constituents of purity better than 99.99% by remelting in an arc furnace into spheres of about 6 mm diam. Undercooling conditions were established in an electromagnetic levitation apparatus described elsewhere¹¹ under clean environmental conditions. The temperature of the sample was monitored in absolute terms by a two-color pyrometer with an accuracy of ± 3 K at a sampling rate of 100 Hz. Additionally, the image of the levitated molten drop was focused onto two silicon photodiodes [Fig. 1(a)], which allowed a relative temperature measurement during the rapid recalescence phase with a time resolution of 1 μ s.¹² In a typical observation cycle, the melt was undercooled to a predetermined temperature and crystallization was initiated by a solid needle at a well defined point in a plane normal to the viewing direction. Solidification proceeded radially from the trigger point, as confirmed by micrographs and indicated schematically in Fig. 1(b). The corresponding recalescence signal as

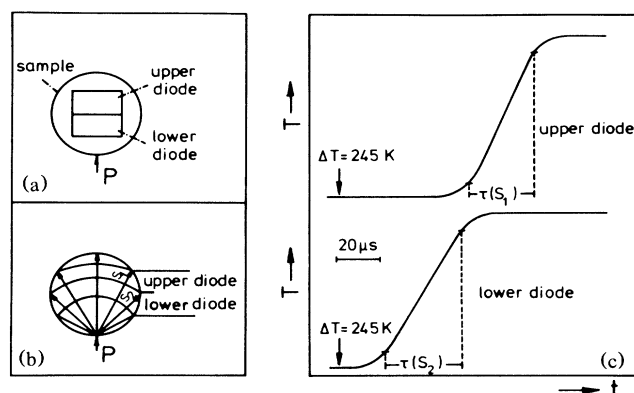


FIG. 1. Principle of the measurement of solidification velocity in levitated undercooled drops. (a) An image of the sample is focused onto two fast-responding photodiodes. (b) Solidification is initiated intentionally at point P, from where it proceeds radially and is registered by the two diodes consecutively. (c) Typical output trace of the two photodiodes, shifted vertically for clarity.

recorded by the two sensor elements is shown in Fig. 1(c). Considering the path length difference s [Fig. 1(b)], the velocity of the thermal front can be derived independently for the two detectors, and turns out to be constant throughout the sample. The decay length of the thermal front is small compared to the sample dimensions as confirmed by the sharp transition between the lower and upper diode output [Fig. 1(c)], so the observed signal can be related directly to the dendrite tip velocity.

Results for a measurement of the solidification rate as a function of undercooling are shown in Fig. 2 for a sample of pure Ni. Considerable solidification rates up to 70 m/s are observed at the highest undercooling values $\Delta T = 324$ K. At ΔT less than a critical limit, $\Delta T^* = 175$ K, the data follow a power law $V \sim \Delta T^\beta$ with $\beta = 3$, whereas for undercooling values larger than ΔT^* a linear dependence is found. Such an apparent break in the growth conditions has been observed earlier by Walker.¹³

A theoretical calculation of the solidification velocity as a function of undercooling for pure nickel is indicated by the solid line in Fig. 2. This function has been derived in a calculation considering both the dissipation of the enthalpy of crystallization into the undercooled melt ahead of the solidification front and the influence of the dendrite tip curvature. The total undercooling T is thus expressed by

$$\Delta T = \Delta T_i + \Delta T_r = (T_i - T) + (T_m - T_i), \quad (1)$$

where the thermal undercooling ΔT_i is the difference between the temperature of the dendrite tip, T_i , and the melt temperature T far away from the dendrite. ΔT_r is the depression of the melting point below the equilibrium value T_m due to the Gibbs-Thomson effect arising from

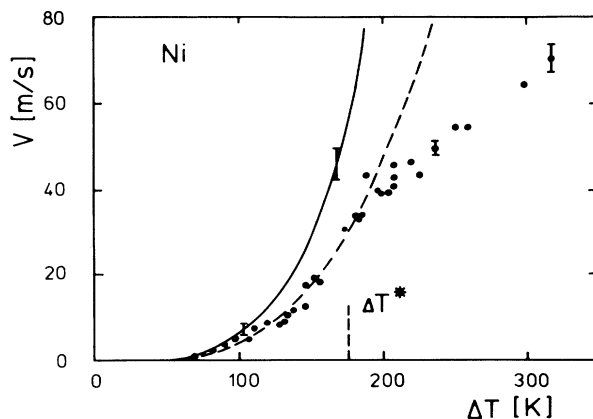


FIG. 2. Growth velocity as a function of undercooling for primary solidification of pure Ni. Dots, measured values; solid line, theoretical prediction according to Ref. 2 (error bar marks uncertainties in material parameters used); dashed line, theory including nonequilibrium at the interface by introducing atomic attachment kinetics.

TABLE I. Material parameters of Ni and $\text{Cu}_{70}\text{Ni}_{30}$ as used in the calculations of dendritic growth.

Parameter	Dim.	Ni	$\text{Cu}_{70}\text{Ni}_{30}$
Heat of fusion	J/kg	2.922×10^5	2.317×10^5
Specific heat	J/kgK	735	576
Interface energy	J/m ²	0.464	0.374
Thermal diffusivity	m ² /s	6.5×10^{-6}	3.0×10^{-6}
Liquidus slope	K/at. %		4.38
Distribution coefficient			0.81
Diffusion coefficient	m ² /s		6.0×10^{-9}
T_0 temperature	K		1471

the curvature of the dendrite tip.² Together with a stability criterion¹⁴ based upon linear stability analysis,¹⁵ the development of Eq. (1) by Liptons, Kurz, and Trivedi² leads to an expression for the tip velocity as a function of undercooling which is free of adjustable parameters. In the calculated function (solid line, Fig. 2), material parameters as listed in Table I have been used. The error bar in Fig. 2 indicates the variation arising from uncertainties in these parameters.

A comparison to the measured values indicates a systematic overestimate of the growth velocity. A much better agreement is obtained, at least for $\Delta T < \Delta T^* = 175$ K, if the assumption of local equilibrium at the interface is relaxed by adding a kinetic term $\Delta T_k = V/\mu$ to the right-hand side of Eq. (1). Here V is the interface velocity and μ is a coefficient describing the atomic attachment kinetics at the interface.¹⁶ The dashed line in Fig. 2 was fitted to the experimental results with $\mu = 1.6$ m/sK. This compares well to a value of $\mu = 1.4$ m/sK derived from the collision-limited growth model,¹⁷ using

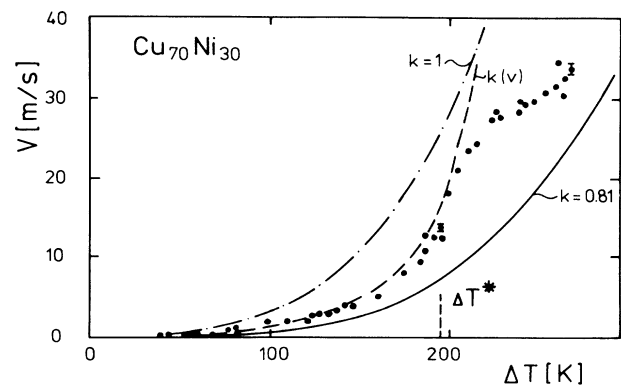


FIG. 3. Growth velocity as a function of undercooling for primary solidification of a $\text{Cu}_{70}\text{Ni}_{30}$ alloy. Dots, measured values; solid line, theoretical prediction according to Ref. 2, using the equilibrium partition coefficient $k = 0.81$; dash-dotted line, same calculation for $k = 1$ (partitionless solidification); dashed line, theory including solute trapping by using a velocity-dependent partition coefficient (Ref. 19).

known material constants only. Good agreement can thus be concluded between theoretical calculations and experimental growth velocities for pure Ni in the undercooling range below ΔT^* , provided the condition of local interface equilibrium is relaxed. Similar conclusions have been drawn by Coriell and Turnbull¹⁸ in their analysis of Walker's¹³ data. No agreement with present theories is found for undercooling levels larger than ΔT^* .

The corresponding results for the alloy system Cu₇₀-Ni₃₀ are shown in Fig. 3. A behavior qualitatively similar to the pure metal is observed with overall reduced solidification velocities. Growth rates for an alloy can be calculated in a way similar to Eq. (1) by adding a term ΔT_c describing the solutal undercooling due to the concentration gradient ahead of the dendrite tip:²

$$\Delta T = \Delta T_l + \Delta T_r + \Delta T_k + \Delta T_c. \quad (2)$$

The result of such a calculation is shown by the solid line in Fig. 3, which is marked by the equilibrium partition coefficient $k = 0.81$ of the alloy used.

In contrast to the pure metal, Fig. 3 shows an underestimate of growth velocity by the theoretical data. This must be related to solutal effects. Indeed the situation is reversed if local solutal equilibrium at the interface is completely disregarded, i.e., the partition coefficient is set equal to unity (dash-dotted line, Fig. 3). The experimental data are found between the limits $k = 0.81$ (equilibrium) and $k = 1$ (partitionless solidification), which suggests a situation where growth velocities are too high to establish diffusional equilibrium but not yet sufficiently fast for completely segregation-free solidification.

A model describing the transition between solutal equilibrium and partitionless solidification has been developed by Aziz¹⁹ in the form of a velocity-dependent partition coefficient $k_v(V)$:

$$k_v = \frac{k + (a_0/D)V}{1 + (a_0/D)V}, \quad (3)$$

where D is the diffusion coefficient in the melt and a_0 is a length scale of the order of the interatomic distance. This was introduced by Liptons, Kurz, and Trivedi² in the calculation of the free dendritic growth velocity, leading to the dashed line in Fig. 3 for $a_0 = 3 \times 10^{-10}$ m. The agreement with the experimental data suggests a transition from the equilibrium situation of a solidification controlled essentially by the solutal gradient to a thermally controlled growth, which is due to a relaxation of diffusional equilibrium in the solid-liquid interface.

The data presented here demonstrate that rapid solidification of a pure metal or an alloy may be described by the current theories at least for undercooling levels smaller than a limit ΔT^* , provided the conditions for local equilibrium at the solid-liquid interface are relaxed. For pure metals, it suffices to include the effects

of atomic attachment kinetics at the interface. Here the increased front velocity disturbs the solidification-melting equilibrium by reducing atomic transport from the solid back into the liquid. This decreases the transport of heat from the interface into the melt and thus requires a higher undercooling to sustain the growth rate. In alloys, the condition of diffusional equilibrium is gradually becoming less important with increasing solidification velocity. Therefore, solute rejection is reduced and solutal undercooling decreases as the interface concentration approaches the melt composition. This ultimately leads to partitionless solidification which is solely controlled by the thermal gradient.

Above a certain undercooling temperature, ΔT^* , the growth kinetics change from an exponential law to a linear undercooling dependence. This behavior is not described by present theories. It should be noted that the transition temperature, ΔT^* , coincides with the critical undercooling for grain refinement.¹² This marks a sharp undercooling value where the final solidified product suddenly changes from coarse- to fine-grained morphology. Willnecker, Herlach, and Feuerbacher²⁰ have shown, by observing (Cu-Ni) alloys with varying atomic mobility (introduced by adding small amounts of boron), that this transition is related to a critical growth velocity rather than a critical undercooling temperature. Besides these observations, no interpretation is presently available for the growth behavior beyond ΔT^* .

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