# Experimental Evidence for Dendrite Tip Splitting in Deeply Undercooled, Ultrahigh Purity Cu

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In a recent paper we used a phase-field model of solidification in deeply undercooled pure melts to show that a kinetic instability could result in dendrite tip splitting, and we speculated that such tip splitting could give rise to the phenomenon of spontaneous grain refinement. Here we present evidence, from the as-solidified microstructure of deeply undercooled ultrahigh purity Cu, of what appears to be dendrite tip splitting during recalescence. The significance of this finding in a nongrain refined sample is discussed in terms of the current theories for spontaneous grain refinement.

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*Introduction.*—Spontaneous grain refinement in undercooled pure melts has been a phenomenon of enduring interest since it was first reported to occur in Ni by Walker [1] in 1959. At a well defined undercooling, $\Delta T^* = 140$–$150$ K, Walker observed an abrupt transition from a coarse columnar grain structure to a fine equiaxed structure, with a reduction in grain size of at least 1 order of magnitude. This effect has subsequently been identified in other pure metals [2,3] and in a range of alloy systems [4–6].

The origins of the effect are controversial, although there seems to be general consensus that dendrite fragmentation is involved either during [7,8] or immediately after [9,10] recalescence. The occurrence of a discontinuity in the growth velocity-undercooling curve [2,11] coincident with the onset of grain refinement would tend to suggest the former of these possibilities is more likely, as would an apparent change in the morphology of the growth front revealed by high-speed imaging [12]. One possibility is some form of kinetically induced growth instability [7,8] at the dendrite tip. This may result in the growth of an unstable structure [13] during recalescence that subsequently remelts to give the observed grain refined microstructure.

In a previous paper [14] we used a phase-field model for the solidification of a pure material to propose a model for spontaneous grain refinement based on repeated multiple tip splitting. This model showed that as the undercooling (or, equivalently, growth velocity $V$) is increased the perturbations that initiate sidebranching move closer to the dendrite tip. Eventually, such perturbations approach within $(1$–$2)R$ of the tip, where $R$ is the radius of curvature at the tip. This gives rise to a highly distorted dendritic structure. Any increase in the growth velocity beyond this point results in splitting of the dendrite tip and the formation of double fingers or doublons [15], an example of which is shown in Fig. 1. Such morphologies have been observed experimentally in transparent analog casting systems for both two-dimensional [16] and three-dimensional [17] solidification and in both cases results in the formation of a characteristic "seaweed" morphology [18].

We found that for values of the kinetic parameter $\mu$ of the order $1.4\ \mathrm{s\,m^{-1}\,K^{-1}}$ the onset of tip splitting within our phase-field model occurred at growth velocities comparable to those at which grain refinement is observed in pure Ni, by far the most widely studied material with respect to grain refinement. This would tend to support the idea that the phenomena of dendrite tip splitting and grain refinement are related.

The value of the kinetic parameter used was estimated from the theory of atomic attachment as given by Turnbull [19]

$$\mu = f\frac{V_0 \Delta H}{RT_{lm}^2},$$

where $\Delta H$ is the molar heat of fusion, $R$ is the gas constant, and $V_0$ is the velocity of sound in the liquid. $f$ is a packing fraction less than unity which, for close-cubic packed metals, is approximately 0.5. A similar value was used by Willnecker *et al.* [2]. All other parameters within our model were chosen so as to be appropriate for pure Ni.

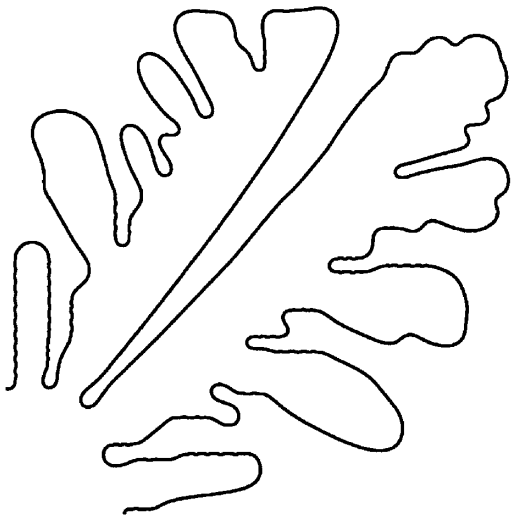

FIG. 1. Example phase-field calculation showing the morphology of a dendrite subject to kinetically induced tip splitting (after Ref. [14]).

  

However, recently molecular dynamic simulations of the solid-liquid interface [20] have suggested that Turnbull's method may significantly overestimate $\mu$. Hoyt *et al.* give $\mu = 0.52\ \mathrm{s\,m^{-1}\,K^{-1}}$ for growth along the $\langle 100 \rangle$ direction in Ni, with a kinetic anisotropy $\varepsilon_k$ of 0.13. Using these parameters Bragard *et al.* [21] find no evidence of dendrite tip splitting in their three-dimensional phase-field models of Ni, up to the highest growth velocities observed in Ni (growth velocities up to $90\ \mathrm{m\,s^{-1}}$ were simulated compared to maximum growth velocities in Ni of around $70\ \mathrm{m\,s^{-1}}$ at $\Delta T = 325$ K [2]). However, they do note that for lower values of the kinetic anisotropy tip splitting can be the dominant growth mode.

In this Letter, we present experimental evidence from deeply undercooled high purity Cu, which we believe supports the idea of dendrite tip splitting at high undercooling, and discuss the implication of this result for the theory of grain refinement.

*Experimental method.*–Melt fluxing was chosen as the most suitable means to study the undercooling behavior of pure Cu. The method allows high undercoolings to be achieved as nucleation on the container walls is prevented by isolating the melt from these surfaces. The flux can also aid the removal of oxide impurities from the melt by dissolution into the glass and protects the surface from oxidation.

Undercooling experiments were performed within a stainless steel vacuum chamber evacuated to a pressure of $10^{-6}$ mbar and backfilled to 500 mbar with $N_2$ gas. Spherical samples of 6–8 mm in diameter were heated, in silica crucibles, by induction heating of a graphite susceptor contained within an alumina radiation shield. Viewing slots were cut in the susceptor and alumina to allow the sample to be viewed during the experiment. A commercial soda-lime glass was employed as the flux. The temperature was monitored by means of a *k*-type thermocouple positioned at the base of the crucible, which had been thinned, so as to reduce thermal lag. Solidification of the sample is triggered by means of a thin alumina needle which can be pushed through the flux, thus touching the surface of the sample. A schematic diagram of the fluxing apparatus is shown in Fig. 2.

Copper samples of 99.9999% purity (metal basis) were obtained from ALFA (Johnson Matthey). However, as received, these samples contain a residual level of oxygen, $[\mathrm{O}]_{\text{as-received}}$, determined by electrical resistivity measurements to be typically 600–800 ppm. During undercooling experiments, the level of oxygen in the sample will fall as the sample equilibrates with the oxygen partial pressure in the chamber. We have previously found [22] that for Cu the final oxygen content in the as-solidified sample varies with the holding time above the liquidus temperature as

$$[\mathrm{O}]_{\text{final}} = [\mathrm{O}]_{\text{base}} + [\mathrm{O}]_{\text{as-received}} \exp\{-0.025 t_{\text{hold}}\},$$

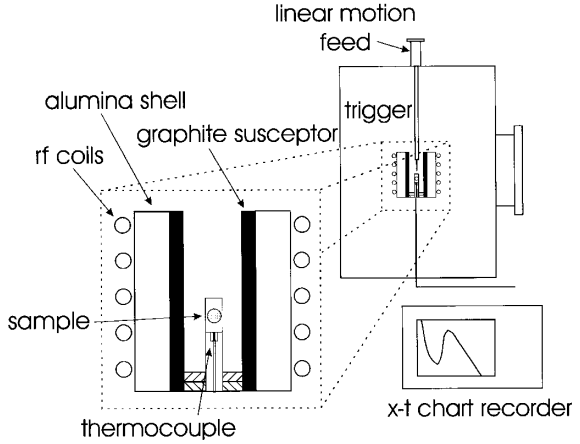


FIG. 2. Schematic diagram of the apparatus used to obtain high undercoolings in Cu by melt fluxing.

where $[\mathrm{O}]_{\text{base}}$ is the base level of oxygen in the chamber and $t_{\text{hold}}$ is the holding time. Although this has not been measured directly, $[\mathrm{O}]_{\text{base}}$ is likely to be relatively low due to the presence of the hot (1400 K) graphite susceptor in the chamber. Electrical resistivity measurements on our deeply undercooled Cu samples indicate that $[\mathrm{O}]_{\text{final}}$ is around 60 ppm.

After undercooling, the as-solidified droplets were mounted in Bakelite and cut to reveal the interior, which was then polished with progressively finer diamond paste to produce a smooth surface. This was then etched in acidified potassium dichromate solution. The solubility of oxygen is much lower in solid copper than it is in the liquid phase and, therefore, during solidification the residual oxygen in the copper will partition from the growing solid into the remaining liquid. Consequently, the liquid that solidifies last will have a higher oxygen content than that which solidified earlier. During the etching process, the oxygen rich and oxygen deficient copper dissolve at different rates, so that the remnant dendritic structure is revealed as a topographic contrast on the polished surface. This is then imaged using differential interference contrast (DIC) mode optical microscopy, a technique which emphasizes topographic relief.

*Results and discussion.*—Figure 3 shows a micrograph of a Cu sample undercooled by 280 K prior to nucleation of solidification. As discussed above, this is a two-dimensional section of a three-dimensional body. Solidification of this sample was triggered and, consequently, the growth direction is known to be from the bottom left corner towards the top right corner of the area imaged. The sample shows numerous ridges or channels [23] that periodically fragment and which we will suggest below are indicative of the growth of dendritic seaweed. In particular, we observe the following: (i) The feature at (1) clearly splits into two, with the two new branches growing in different directions to the original feature; (ii) the feature at (2) appears to split and the two branches

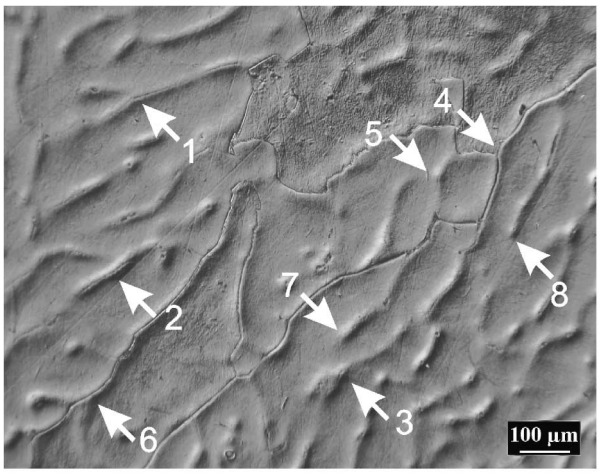


FIG. 3. Micrograph of Cu undercooled by 280 K below the equilibrium liquidus temperature before solidification by triggering with an alumina needle. The direction of the solidification front was from top right to bottom left in the figure. The microstructure appears to show numerous features that can be associated with dendrite tip splitting.

FIG. 4. Simulation of the growth of the seaweed morphology (solid shown light grey) with remnant liquid channels highlighted (after Ref. [16]).

diverge and then continue to grow parallel; (iii) a similar effect can be seen at (3) but with much smaller spacing; (iv) the feature at (4) splits and the two branches then grow parallel until one of the branches splits again at (5); (v) the feature at (6) seems to undergo a threeway split, with the center branch splitting again soon after.

Similar structures have also been observed at $\Delta T = 293$ K, although at undercoolings above 310 K, recrystallization and recovery of the sample during the postrecalescence period tends to obscure observations of this type of structure.

We suggest here that the features observed in the micrograph are the remnant liquid channels that remained after the initial growth of dendritic seaweed from the highly undercooled melt. This can most easily be seen by comparing the features on the micrograph with the simulation of seaweed growth shown in Fig. 4 (after Ref. [16]). For direct comparison the growth of the solid (light grey) in this figure is also from the lower left corner towards the upper right corner. Other features on the micrograph would tend to confirm this interpretation. First, all the channels appear to be of approximately the same width, a well established feature of the growth of the seaweed morphology. Second, the grain boundaries (sharp lines reminiscent of a crack in the microstructure) tend to follow the channels. This is what would be expected if the channels delineated the remnant liquid following the growth of the seaweed morphology, as these would represent the interface between regions with differing crystallographic orientations. Within this picture, the spontaneous appearance of a channel, such as at the points marked (7) or (8) on the micrograph, would delineate the location at which a tip-splitting event occurred.

Growth velocities in pure Cu have to date been measured [6] up to $\Delta T = 250$ K, as shown in Fig. 5. Unfortunately, we have not yet been able to extend our growth velocity measurements to include $\Delta T = 280$ K, but the data available do allow us to estimate the likely growth velocity. At undercoolings above 90 K, the data follow a power-law curve with a very high degree of confidence ($R^2 = 0.9897$). Assuming the power-law relationship continues to hold, we may extrapolate from the highest measured velocity (97 m s$^{-1}$ at $\Delta T = 250$ K) to obtain an estimate of the growth velocity at $\Delta T = 280$ K of 124 m s$^{-1}$. This is significantly higher than the maximum growth velocity simulated by Bragard *et al.* [21]

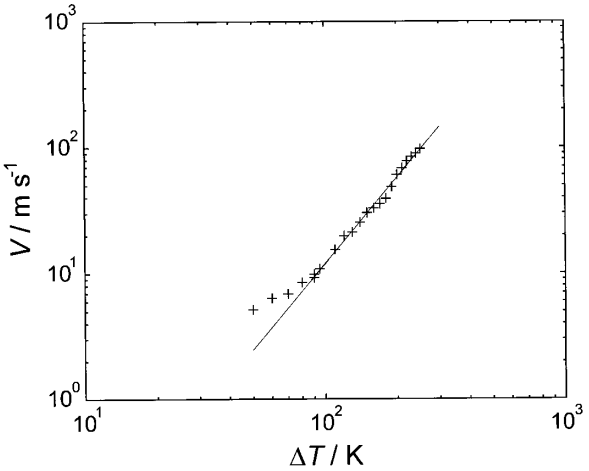


FIG. 5. Measured dendrite growth velocities in deeply undercooled pure Cu (after Ref. [6]).

and, consequently, not inconsistent with recent phase-field models even if very high kinetic anisotropies are assumed.

In our previous paper, we suggested that repeated multiple tip splitting may be the underlying mechanism for grain refinement in materials solidified from deeply undercooled. If Fig. 3 is indeed indicative of dendrite tip splitting in a nongrain refined material, then this model clearly needs to be reconsidered. One possibility is simply that the transition to the seaweed morphology is totally unconnected with grain refinement and that in most materials grain refinement occurs at a lower undercooling, thus masking the evidence for this phenomenon.

However, an alternative hypothesis is that tip splitting does indeed give rise to dendrite fragmentation and hence grain refinement, but only in the presence of a solute. This might occur as the result of the nonequilibrium solute concentration due to solute trapping driving a remelting of the seaweed structure, in a manner similar to that suggested by Karma [10]. In this case, we could then argue that grain refinement has not occurred in this particular sample because of the very pure nature of the material, in particular, the very low oxygen concentration. This is not necessarily inconsistent with previous reports in the literature of grain refinement in "pure" materials. All materials will have some residual level of impurity, particularly if we consider gaseous species such as $O_2$ and $H_2$. It then simply becomes a question of what purity of materials is required in order to inhibit grain refinement and preserve the evidence for the growth of the seaweed morphology in the as-solidified microstructure. A consequence of this model would be that grain refinement would not be observed in truly pure materials. As far as we are aware, none of the authors reporting grain refinement in pure Ni has reported either the residual oxygen or hydrogen concentrations in their samples. The latter may be significant as undercooling experiments on Ni, which are usually performed by electromagnetic levitation, often utilize a reducing ($H_2$-rich) atmosphere to inhibit surface oxide formation. With this in mind, further studies of the solidification of deeply undercooled, ultrahigh purity melts should be given the highest priority.

*Conclusions.*—The microstructure of an ultrahigh purity Cu sample solidified from its parent melt at an undercooling of 280 K has been presented which shows strong evidence that the initial solidification morphology was that of dendritic seaweed. This would represent the first observation of this type of morphology in a metal. We propose that this type of growth morphology is actually quite common in deeply undercooled metallic melts, but that normally the presence of nonequilibrium solute concentrations will cause the seaweed structure to remelt after recalescence, giving rise to the familiar phenomenon of spontaneous grain refinement. In this particular sample, the exceptionally high purity of the material, particularly with regard to oxygen, has inhibited remelting, thus preserving evidence of the growth of the seaweed morphology. This model would account for the observation that spontaneous grain refinement is accompanied by a change in the growth front morphology, as revealed by high-speed imaging of undercooling experiments [12].

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