

# **Experimental Investigation and Simulation of Non-Equilibrium Solidification**

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## **ABSTRACT**

Welding conditions, particularly those prevalent during high energy density beam processes, often lead to non-equilibrium solidification effects. Traditional solidification theories and models can take many of these effects into account, and can predict solidification microstructures, temperatures, and compositions. Sample calculations using these models are presented. An alternative approach to study solidification behavior during welding, using computational thermodynamics and kinetics calculations, will also be discussed. Finally, recent results of *in-situ* experiments that directly show non-equilibrium solidification in a commercial low alloy steel weld will be illustrated. Additionally, the paper will describe current limitations and needs for future work in order to better model non-equilibrium solidification behavior.

## **INTRODUCTION**

True equilibrium solidification requires very low cooling rates and growth rates and is rarely found in commercial processes such as welding. Instead, non-equilibrium solidification takes place. There are varying degrees to which non-equilibrium can take place. Solute partitioning during solidification can lead to microsegregation and to the formation of non-equilibrium phases at the latter stages of solidification. Such Scheil-like behavior is common in welds. At higher growth rates, non-equilibrium partitioning may take place. For high-energy density processes such as laser welding and electron beam welding, where thermal gradients are large and cooling rates are high, such non-equilibrium partitioning may be found. Finally, competition among different solidification modes may take place, resulting in the suppression of the most stable phase and the solidification of more kinetically favorable phases. Such effects have been found often in stainless steels<sup>1</sup>. In order to understand the microstructure development during welding, an understanding of non-

equilibrium transformation behavior is necessary. This paper will briefly describe the current status of solidification theory and a few sample calculations will be presented. Alternate approaches to describe non-equilibrium solid state transformation behavior, that provide added insight into microstructure development, will be discussed. Outstanding needs in the application of the theory to weld solidification in real systems will be noted. The remainder of the paper will cite new experimental results in which non-equilibrium solidification was detected *in-situ*.

## SOLIDIFICATION THEORY INCLUDING NON-EQUILIBRIUM EFFECTS

The description of solidification behavior, from low growth velocity, steady-state planar growth to cellular/dendritic growth at intermediate speeds and to non-equilibrium planar growth at high speeds, is reasonably well-developed<sup>2</sup>. Low growth velocity, steady-state planar growth will not be considered in this paper because it has little relevance to weld solidification, which normally occurs at higher growth velocities. The cellular/dendritic growth at intermediate velocities can be described mathematically by considering the solute diffusion behavior around a dendrite tip and combining this with dendrite stability theory. At even higher growth rates, when the growth velocity exceeds the absolute stability limit ( $v_a$ ), planar growth prevails, although a growth front instability may produce a banded structure over a limited range of velocities beyond  $v_a$ . The solution of the planar growth problem is considerably simpler than the dendritic/cellular growth problem since steady state growth requires that the solid forms at the overall alloy composition  $C_0$ .

As the growth velocity increases, non-equilibrium partitioning between the parent liquid and the product solid must be taken into account. Several formalisms have been proposed to allow for the deviation of the partition coefficient  $k_v$  (= solid composition/liquid composition) from the equilibrium value,  $k_0$ , to a value of 1, which represents partitionless transformation behavior. The most common expression used is that proposed by Aziz<sup>3</sup>. In solving the growth problem, both the solid and liquid compositions at the solidification interface must be known. Therefore, in addition to describing the velocity dependence of  $k_v$ , one needs another relationship to determine both velocity dependent compositions. This can be accomplished by quantifying the change in either the liquidus or solidus slope as a function of velocity. The description given by Boettinger et al<sup>4</sup> is frequently used, although this was derived for the case of dilute solutions only. Recently, a

symmetric collapse of the liquidus and solidus around the  $T_0$  line was proposed<sup>5</sup>. This latter description is convenient to use but it does not have a fundamental basis.

Solidification theory relates the diffusion field at the solidification front to stability theory, taking into account possible non-equilibrium partitioning. Using the equations described in Ref 2, the cellular/dendritic growth problem can be solved, yielding information on the dendrite tip radius, dendrite tip temperature, and the solid and liquid compositions at the dendrite tip as a function of the growth velocity and thermal gradient at the dendrite tip. A plot of this behavior for an Al-2 at % Cu alloy is shown in Figures 1a and 1b. As noted above, the low growth velocity regime, where steady state planar growth is found, has not been considered. At a velocity of roughly 2 m/s, the solid composition at the dendrite tip approaches the overall alloy composition. At this stage, the growth morphology changes, and planar growth prevails as the velocity increases still further. The planar growth regime at high velocities is depicted by the dashed lines in Figure 1a. In the planar growth regime, the calculations indicate that the solid/liquid interface temperature initially increases as the degree of solute partitioning decreases. However, at the highest velocities, interface kinetics become important. The figure shows that the solid/liquid interface temperature decreases with even higher velocities as a consequence of this interface kinetics effect. The change in dendrite tip radius over the range of dendritic/cellular growth is shown in Figure 1b. As the growth velocity increases, the dendrite tip radius decreases until the absolute planar front stability limit is approached.

The velocity dependant partitioning behavior can also be represented in a phase diagram format. Figures 2a and 2b show a portion of the binary Al-Cu phase diagram. The equilibrium liquidus and solidus are shown by dashed lines. In Figure 2(a), a fixed composition  $C_0$  (Al-2 at % Cu) is considered. The liquid/solid compositions are superimposed on the diagram as a function of increasing velocity. Any horizontal line joining the liquidus and solidus traces identifies a compatible set of solidification temperature and corresponding liquid and solid compositions at some growth velocity. The diagram clearly shows the decrease in solute partitioning as the velocity increases, along with the accompanying change in solidification temperature. The region of planar growth is shown by the dotted line. Only the liquid composition is plotted for planar growth since, by definition, the solid composition is fixed at  $C_0$ . The behavior shown in Figure 2(a) for one composition can be combined with calculations for other compositions to produce another non-equilibrium diagram that clearly reveals the change in partitioning, as shown in Figure 2(b). Here,

pairs of lines represent the liquidus and solidus curves at a fixed growth velocity. It should be noted, however, that these non-equilibrium liquidus and solidus curves have limited meaning and cannot be used in the same manner as the equilibrium phase boundaries. For example, for a given composition  $C_0$ , the temperature at which this composition crosses the equilibrium liquidus line represents the temperature below which solidification can begin to take place. In contrast, there is no significance to the temperature at which  $C_0$  crosses the non-equilibrium liquidus corresponding to some given growth velocity. Rather, for solidification to occur at such a fixed growth velocity, some degree of undercooling below this non-equilibrium liquidus must exist, and the liquidus and solidus compositions are given by the compositions at this undercooled temperature. Sample compositions are shown by the X's in Figure 2(b) for the case of  $C_0 = \text{Al-2 at \% Cu}$  and a growth velocity of 1 m/s.

This type of analysis determines the growth rate and growth morphology at the advancing solidification front. In systems where competition between solidifying phases may take place, one would apply the analysis to each phase. It is then assumed that at a given growth velocity, the phase that has a higher growth front temperature will prevail during growth since its solidification front will be ahead of the alternative phase. An example of this approach, in which the competition between ferrite and austenite formation in stainless steels was studied, is given in Refs 5 and 6.

## LIMITATIONS OF CURRENT SOLIDIFICATION THEORIES

Recent attempts to expand solidification theory from binary systems to ternary systems and beyond have simply introduced a linear expansion to identify the liquidus composition as a function of composition<sup>7,8</sup>. Additional terms in the expressions for dendrite tip radius and composition as a function of growth velocity, such as the Peclet number, have been assumed to be constant for all constituents. The extensions to ternary systems were initially based on extrapolating liquidus slopes from binary phase diagrams but in more recent studies, computational thermodynamics has been used to more accurately determine the liquidus slopes and partial derivatives of that slope with respect to individual constituents<sup>5,6</sup>. Such use of computational thermodynamics provides for a more accurate approximation of liquidus surfaces by means of linear extrapolation. Nonetheless, in cases where the liquidus surface is strongly curved, and where the solidification temperature range is large,

such approximations may lead to errors. This is shown schematically in Figure 3, where the liquidus slope is plotted against a generic composition variable. In current methods, the liquidus temperature is calculated based on a linear extrapolation from the liquidus slope at  $C_o$ . In the case where the liquidus slope is strongly curved, and the liquid concentration at the dendrite tip ( $C_L^*$ ) is not very close to the overall  $C_o$  composition, an error in determining the liquidus temperature at  $C_L^*$  corresponding to  $\Delta T$  in Figure 3 will exist. A more recent approach has been to derive the values for the liquidus temperatures directly from computational thermodynamics calculations for all compositions, without relying on linear approximations<sup>9</sup>. It has yet to be shown how much of an improvement in accuracy is achieved by this method.

An integral part of solidification theory is the evaluation of the diffusion problem in the immediate vicinity of the dendrite tip. In most cases, an Ivantsov solution for a paraboloid of revolution geometry is utilized<sup>2</sup>. The assumption of a paraboloid dendrite tip morphology seems to be reasonable and appropriate. However, the Ivantsov diffusion analysis ignores any back diffusion within the solid. For many materials, this assumption is perfectly adequate, and in all cases, the solid state back diffusion contribution is small compared to the diffusion in the liquid. However, for the solidification of non-close packed solids such as BCC ferrite solidification, back diffusion can be substantial<sup>10</sup>. Therefore, it is important to include such effects in the dendrite tip analysis but that capability is unavailable in the analytical models at present.

Finally, in the solidification theories that consider velocity dependant alloy partitioning, which must be considered in many welding applications where growth rates are high, a means for describing the velocity dependant liquidus slope is also required. The theoretical variation of slope with velocity that was described by Boettinger et al<sup>4</sup> is often used although it was derived for the case of dilute solutions. An extended analysis for the case of non-dilute solutions is needed but none is available at present.

## ALTERNATIVE TREATMENT OF NON-EQUILIBRIUM TRANSFORMATION BEHAVIOR

Kinetics computations that are coupled with the computational thermodynamics have also become available in recent years<sup>11</sup>. These approaches solve phase transformation problems by assuming a local equilibrium condition at the moving interface. These programs are directly

integrated with computational thermodynamics routines in order to specify the local equilibrium interface condition in a multicomponent system. This type of kinetics analysis can be used to study dendritic growth or planar front growth. As shown in Figure 4, two different computations can be made, one for sideways growth of dendrites (Figure 4(a)) and the other for planar front solidification (Figure 4(b)). More complex geometries are, at present, not possible because the diffusion kinetics analyses only deal with basically one-dimensional problems (symmetry allows for the solution of cylindrical or spherical geometries as well).

In the case of dendritic growth, one considers the sideways growth of the dendrite in these kinetic analyses rather than the forward growth at the dendrite tip. For cases where the dendrite tip is sharp, and most of the solute rejection at the dendrite tip is to the side of the dendrite and not ahead of the solidification growth front, the geometry in Figure 4(a) is suitable. The advantage of this approach is that the potential for interaction between two neighboring dendrites, in the form of solute profile impingement in the liquid, can be taken into account. This leads directly to a connection between the dendrite arm spacing and the dendritic growth and can provide a direct means for relating dendrite arm spacing to the thermal conditions<sup>12</sup>. Furthermore, solid state diffusion is an integral part of the calculations. Thus, simplifications that are used in Scheil analyses are not necessary. Finally, as a result of the direct coupling of the analysis with computational thermodynamics, the solute enrichment between dendrites and the potential for non-equilibrium phase formation at the latter stages of solidification can be described. Therefore, as part of the solidification analysis, the extent of interdendritic phase formation is also specified. These details are not available in traditional solidification models.

For the case of planar front growth, some means for independently establishing the solute gradient ahead of the front must be included. Otherwise, the kinetic computations are controlled by the numerical features of the calculation, and in particular, the number of nodes in the finite difference or finite element calculation. By assuming the sample is cooled down to the solidus temperature at a fixed rate, the gradients ahead of the solidification are established<sup>13</sup>. It has been shown that steady state planar growth behavior can be simulated by this approach<sup>13</sup>. An example of such a calculation for steady state planar growth in the Al-Cu system is shown in Figure 5. As shown in the figure, a reasonable representation of steady state growth with a constant velocity can be achieved.

There are two main advantages of such computational kinetics calculations. First, multicomponent systems can be readily evaluated, without any limitations or assumptions with regard to the linearity of the liquidus or solidus surfaces, or the positioning of the multi-component tie-lines. Second, these calculations take solid state back diffusion directly into account, and therefore they may be particularly valuable when considering solidification of phases with substantial solid state diffusion rates, such as BCC phases.

However, at present there are several drawbacks to this method of analyzing solidification. First, the thermal conditions are not taken into account. Therefore, one needs to specify independently the variation of volume element temperature with time in Figure 4(a). For planar growth, since a thermal analysis is needed to determine the growth rate, the use of computational kinetics calculations may have limited value.

Another weakness in the computational kinetics calculations is the limitation to one-dimensional diffusion problems. Recent modeling efforts using the phase field method have eliminated this constraint, but the incorporation of multi-component compositions into phase field models is rather difficult. Phase field models also suffer from their extreme computational demands.

Perhaps the biggest drawback to current computational kinetics calculations is the inability to include non-equilibrium partitioning into the computational thermodynamics that define the local equilibrium state at the interface. One recent approach has allowed for the imposition of a para-equilibrium constraint<sup>14, 15</sup>, but a more robust capability is needed before the common non-equilibrium effects found under many welding conditions can be properly taken into account.

## EXPERIMENTAL EVIDENCE OF NON-EQUILIBRIUM SOLIDIFICATION

Non-equilibrium solidification behavior can be manifested in two different ways. First, non-equilibrium partitioning of alloy constituents can take place at the interface. Second, non-equilibrium phases may form during solidification, either in the form of competition among phases at the solidification front or at the later stages in the interdendritic regions. The first phenomenon has been studied extensively and experimental evidence has validated the models for non-equilibrium partitioning at the interface such as the Aziz model. Non-equilibrium phase formation has also been studied. One aspect of non-equilibrium phase formation is the potential for

competitive growth among phases during solidification. This competition has been the subject of recent investigations of stainless steels, where a change in solidification mode during welding, due to non-equilibrium solidification, has been observed. Several researchers have found such a change in solidification mode at high cooling rates, from primary ferrite formation (the equilibrium solidification mode) to primary austenite formation<sup>1</sup>. The change in solidification mode has been studied theoretically by comparing the dendrite growth velocities for ferritic and austenitic growth based on the solidification theories mentioned earlier<sup>6,7,16</sup>. A major hurdle in these analyses is the extension of the solidification theory developed for binary alloys to ternary Fe-Cr-Ni systems that are representative of stainless steels, as discussed earlier.

Recently, the non-equilibrium change in solidification mode has been examined *in-situ* for the first time<sup>17</sup>. Synchrotron irradiation was used to monitor the solidification behavior and to identify directly the non-equilibrium solidification of austenite in an Fe-C-Al-Mn low alloy steel during welding. Under equilibrium conditions, this alloy (Fe-0.23C-0.56Mn-0.26Si-1.77Al-0.003Ti-0.006O-0.064N, all in wt %) solidifies in a primary ferrite mode. With subsequent cooling, some ferrite transforms to austenite in the temperature range of 1600 to 1000K. Still further cooling, to room temperature, results in the transformation of austenite to martensite. When the weld microstructure is observed at room temperature, it is difficult or even impossible to determine what the solidification process was. In contrast, *in-situ* observations allow for the detection of the solidification behavior directly.

The experimental set-up for these studies is shown in Figure 6. A gas-tungsten arc was used to generate a stationary spot weld and the solidification behavior was monitored *in-situ* by focusing a synchrotron beam on the solidifying weld pool and analyzing the scattered intensity. Even under conventional arc welding conditions, the solidification is primary ferrite formation<sup>17</sup>. However, under rapid cooling conditions prevalent during the spot welding conditions shown in Figure 6, a change in solidification mode was observed. Thermal profiles showing the enhanced cooling rate in the spot weld compared to a conventional linear weld are shown in Figure 7. The non-equilibrium solidification behavior is clearly shown in Figure 8, where the scattered intensity is displayed as a function of scattering angle (x-axis) and time (y-axis). It can be seen that immediately after the arc is turned off, a reflection corresponding to austenite is observed while no diffraction peak from ferrite is present. The shift in the position of the austenite (111) peak with time represents the

change in austenite lattice parameter during cooling. After approximately four seconds, the austenite peak disappears and it is replaced by a (110) peak, signifying the solid state transformation of austenite to martensite. The direct observations show unequivocally the non-equilibrium formation of austenite during rapid cooling conditions.

Computational thermodynamics calculations have been used to show that in this multicomponent commercial alloy, the non-equilibrium austenite formation and equilibrium ferrite formation are very close in terms of free energy and stability. Solidification theory was used to try to explain the switch to austenite growth under high cooling rate conditions. Although the theories showed that austenite formation becomes more competitive at higher growth rates, the theory did not predict a switch to primary austenite formation. These results indicate that the current models are still not completely accurate. It is likely that the shortcomings of the theories and models are a result of inaccurate parameters that are used in the calculations.

## SUMMARY and CONCLUSIONS

Non-equilibrium phase transformation behavior is common under many welding conditions. In order to properly understand the microstructural development during welding, a fundamental knowledge of the non-equilibrium solidification behavior is needed. Modern solidification theory can describe many features of dendritic and planar growth under non-equilibrium conditions. However, some shortcomings exist. In particular, there are limitations when considering multi-component systems. Recent advances in computational thermodynamics and kinetics allow for an alternative evaluation of solidification behavior. Although these types of calculations can readily handle multi-component systems, they have their own weaknesses, primarily with regard to the limited ability to consider non-equilibrium partitioning at the solid-liquid interface. Finally, results of recent investigations were presented in which the non-equilibrium solidification of austenite in a low carbon steel was measured directly by *in-situ* experiments.

## ACKNOWLEDGMENTS

This research was sponsored by the Division of Materials Sciences and Engineering, U. S.

Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. The authors would like to thank J. W. Elmer, Lawrence Livermore National Laboratory and M. Quintana, Lincoln Electric Company for help with carrying out the *in-situ* experiments.

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## Figure Captions

- Figure 1 (a) Calculated plot of solidification interface temperature and compositions as a function of growth velocity for Al-2 at% Cu and a thermal gradient of  $10^4$  K/m. The solid lines represent dendritic/cellular growth while the dashed lines represent planar growth beyond the absolute stability limit. (b) Calculated dendrite tip radius as a function of growth velocity for the same alloy and conditions as in (a). Beyond a growth velocity of approximately 2 m/s, planar front growth takes place and the radius becomes infinite.
- Figure 2 (a) Superposition of the interface liquid and solid compositions as a function of interface temperature on the equilibrium Al-Cu phase diagram (light dashed lines). The plot is for an alloy of overall composition  $C_0$  (Al-2at % Cu) under the same conditions as in Figure 1. Dark solid lines represent dendritic/cellular growth while the dotted lines signify planar front growth. Only the liquid composition is shown for planar front growth since the solid composition is fixed at  $C_0$ . (b) Plot of liquidus and solidus lines at fixed velocities (darker lines) superimposed over the equilibrium phase diagram (light dashed line). For composition  $C_0$ , solidification at a given velocity takes place at a fixed location along the non-equilibrium liquidus/solidus, as shown by the X's for a growth rate of 1 m/s.
- Figure 3 Schematic diagram showing possible errors when using linear expansion to describe the liquidus temperature as a function of composition.
- Figure 4 Volume element orientations for (a) sideways growth of dendrites and (b) planar growth.
- Figure 5 Calculated growth rate for Al-4 wt %Cu cooled to the solidus at 10 K/s showing approximately constant steady state growth.

Figure 6 Schematic diagram showing the experimental setup for the *in-situ* observation of solidification by synchrotron irradiation. A stationary weld pool was irradiated with synchrotron irradiation and phase identification of the solidification structure was performed by analyzing the scattered beam in real time.

Figure 7 Thermal profile for spot weld conditions shown in Figure 6 indicating a cooling rate of over 1500 K/s is achieved.

Figure 8 Diffraction intensity versus time showing initial austenite solidification followed by transformation to martensite (labeled “BCC”) after approximately 4 s.

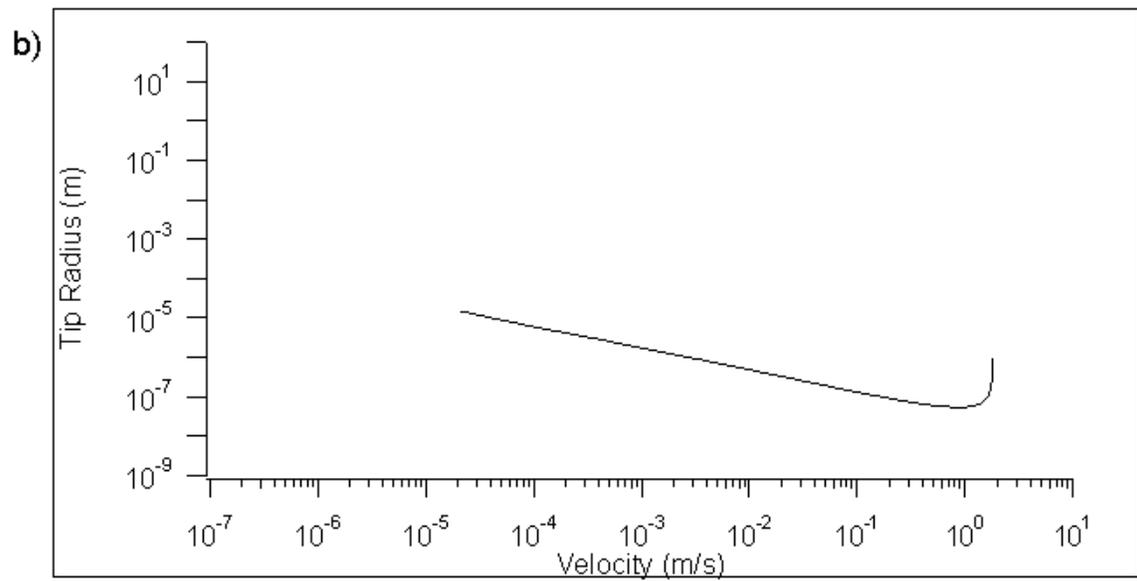
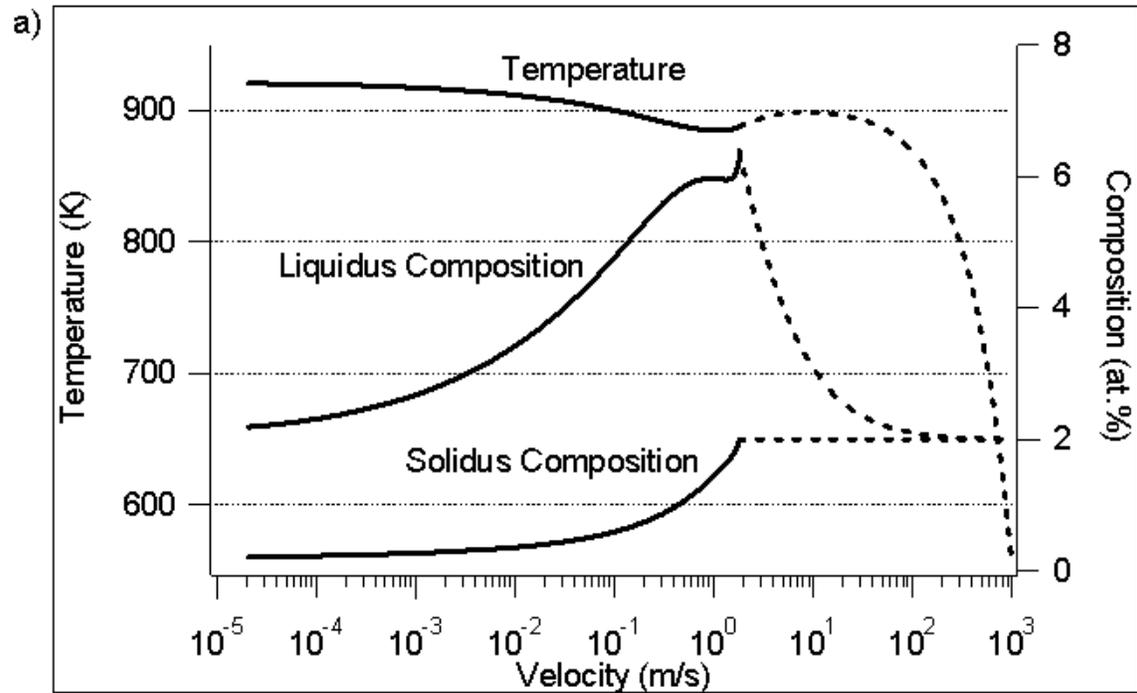


Figure 1

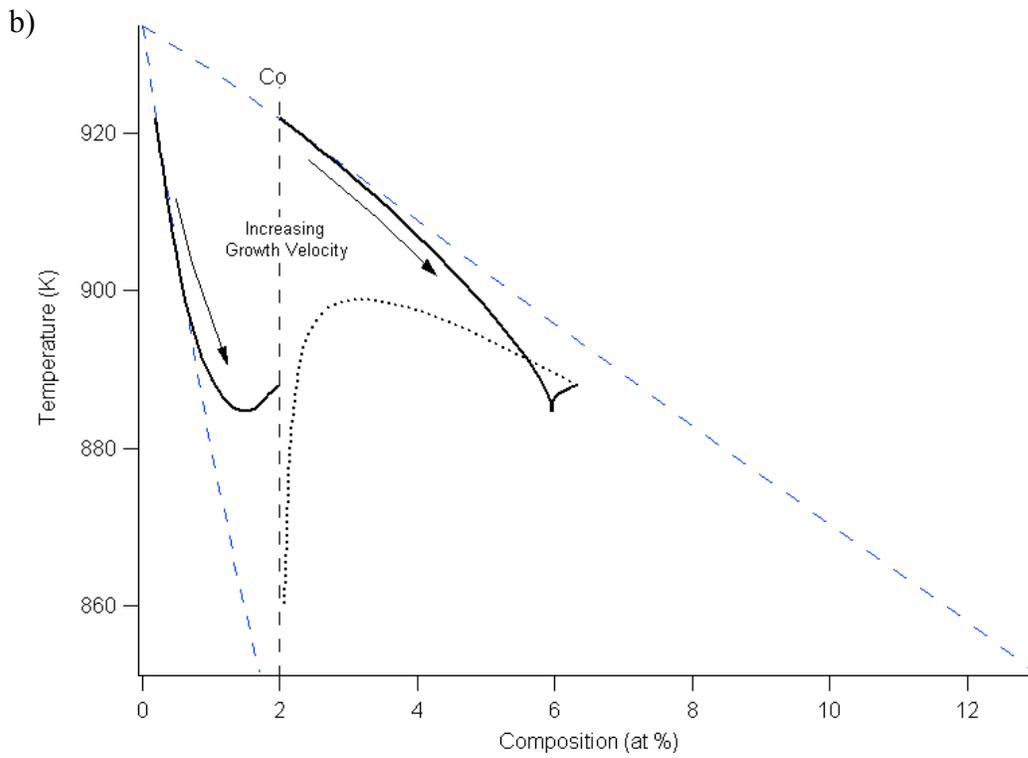
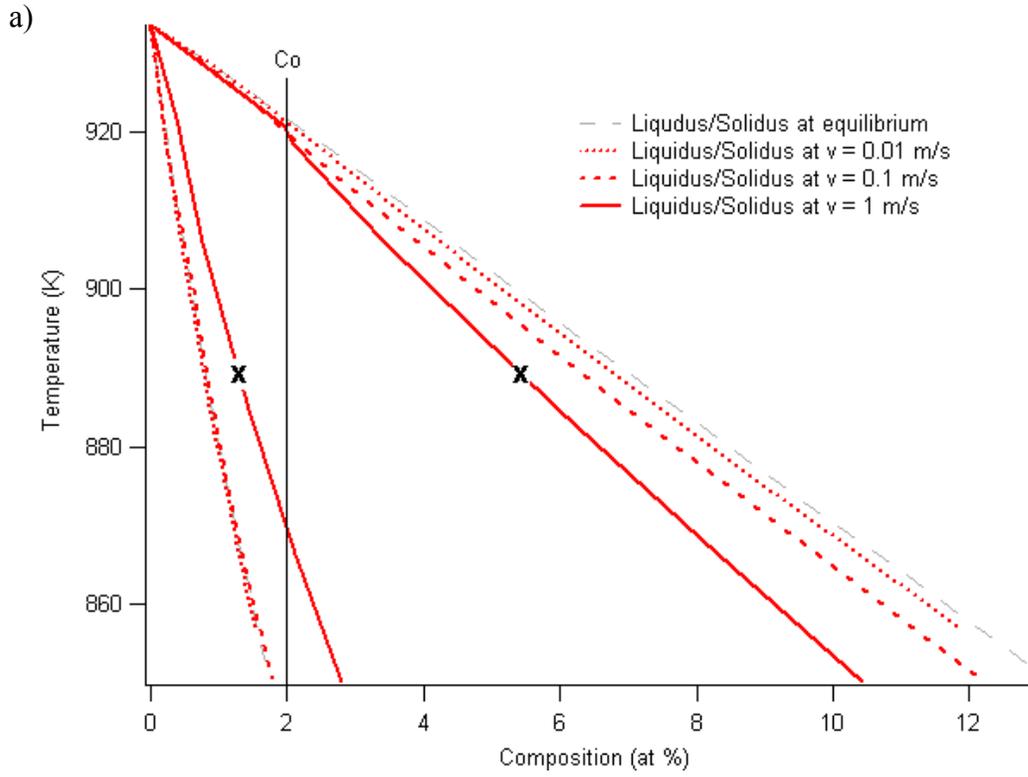


Figure 2

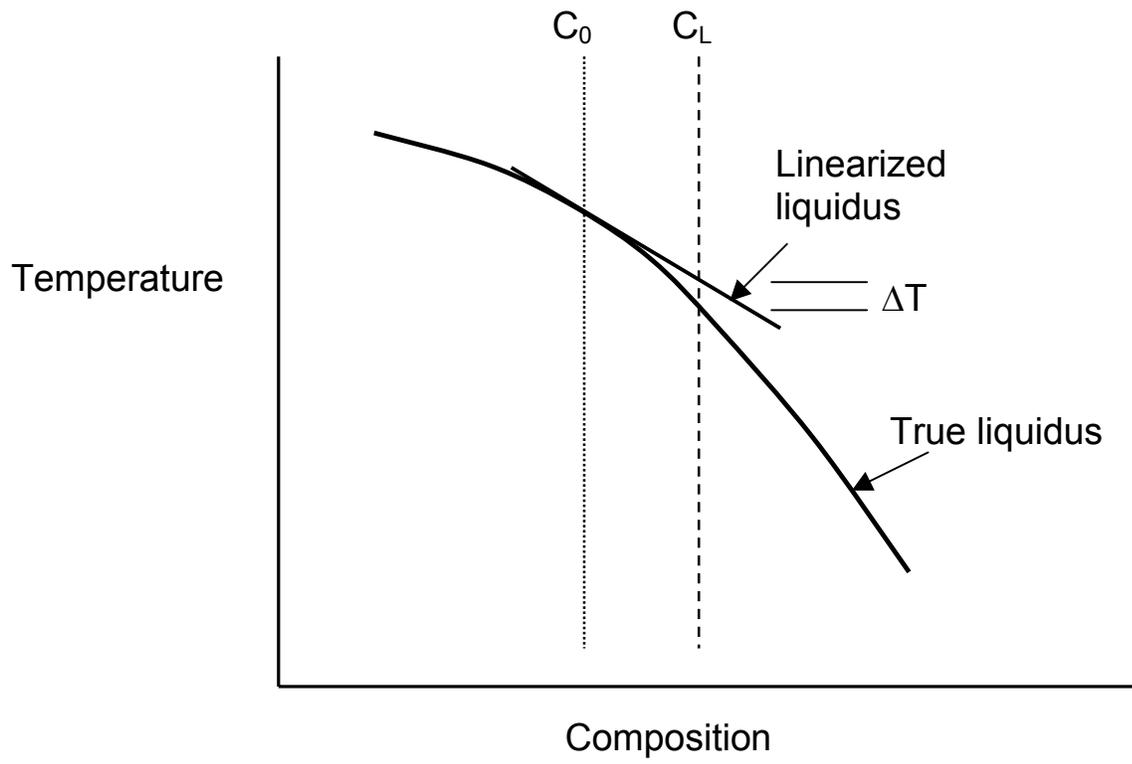


Figure 3

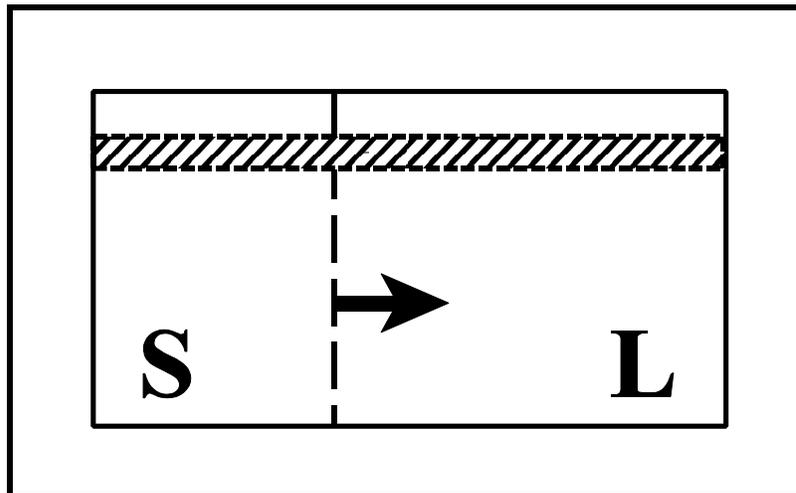
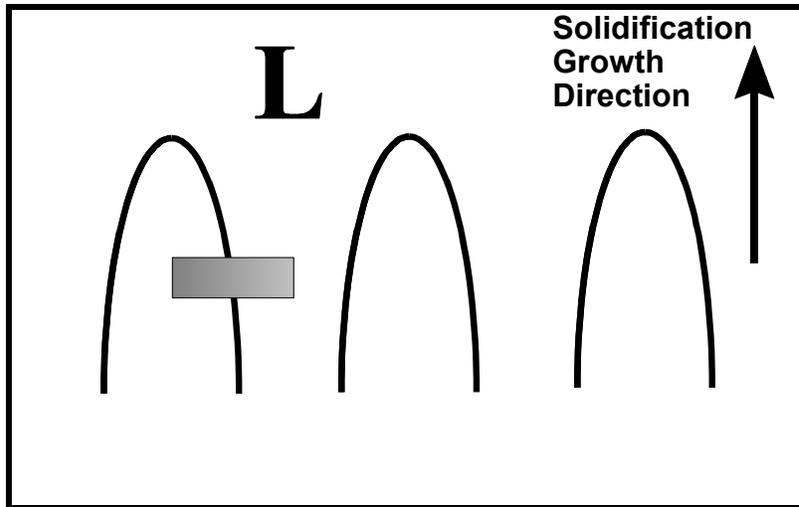


Figure 4

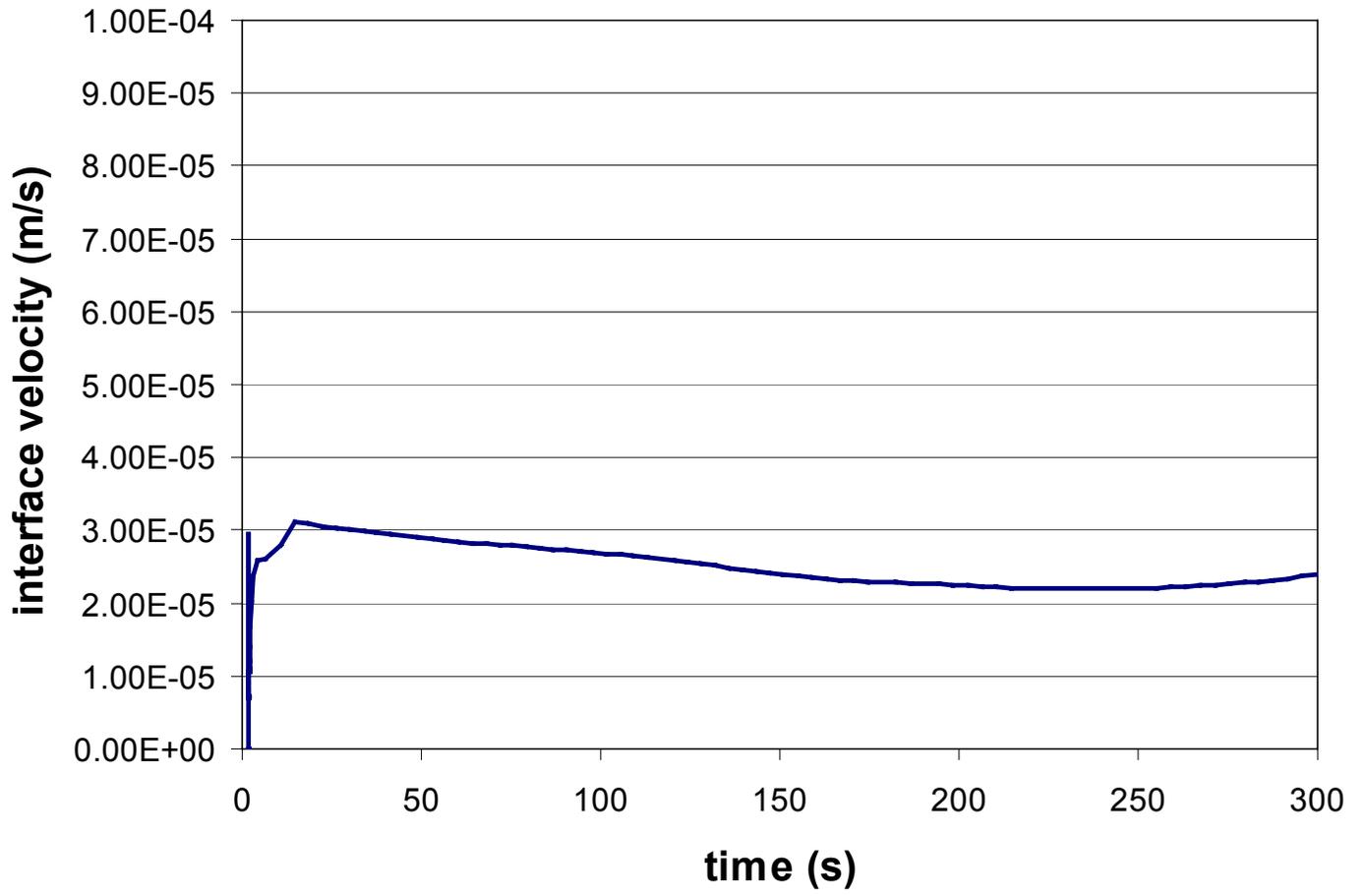


Figure 5

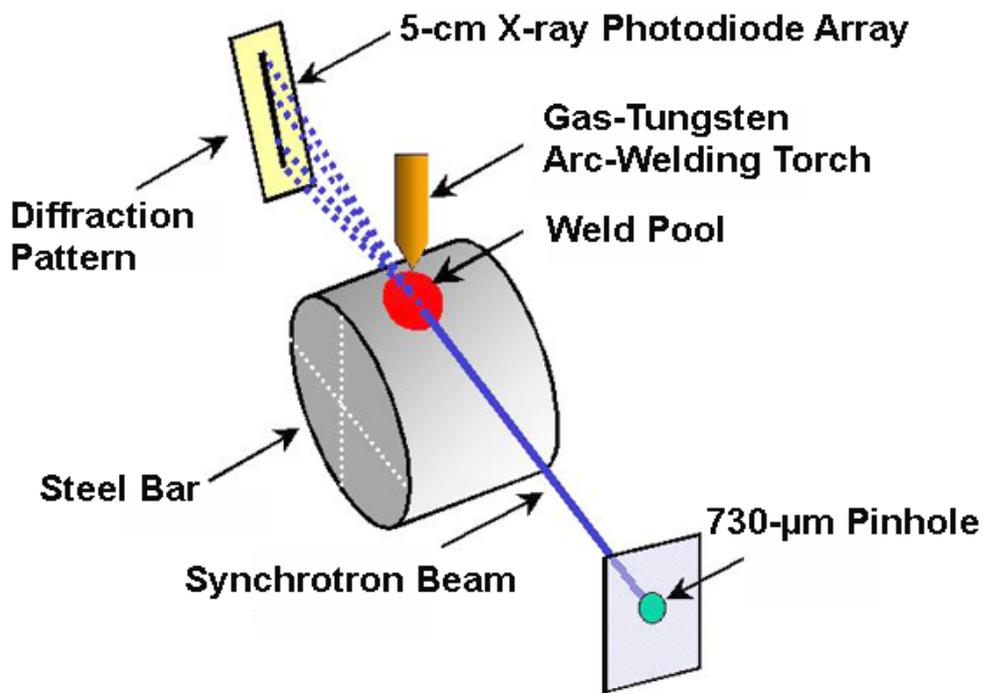


Figure 6

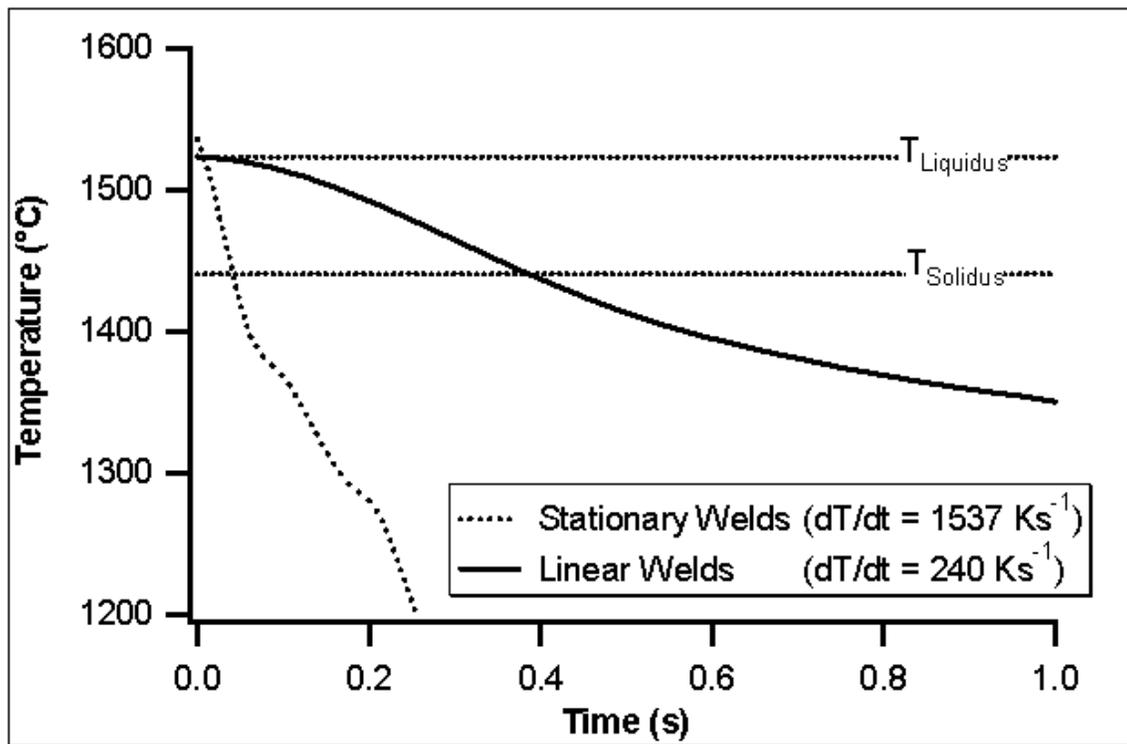


Figure 7

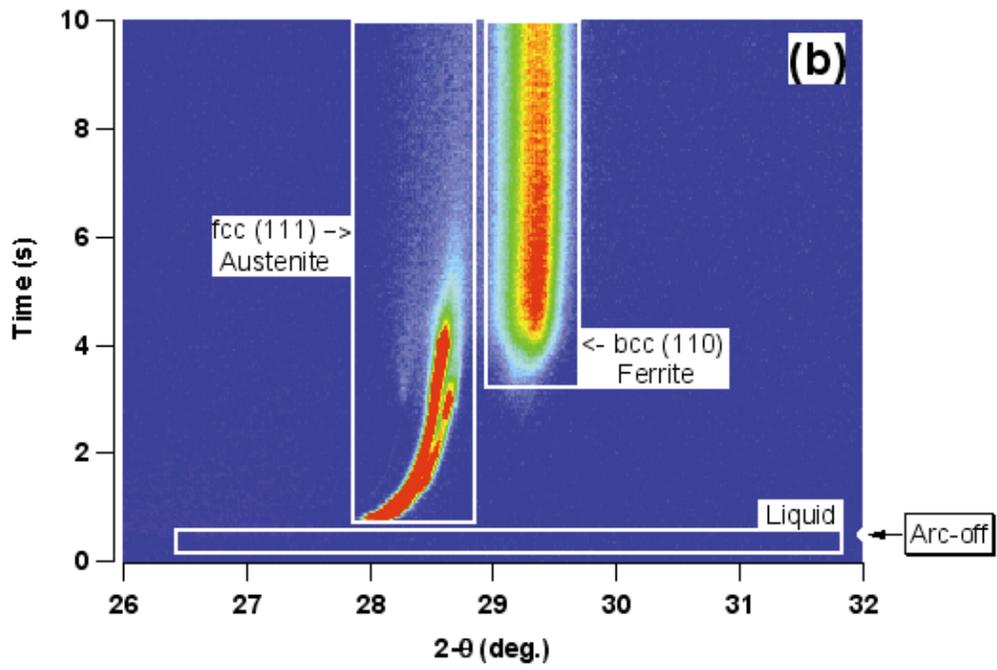


Figure 8