

**EXPLORING SOLIDIFICATION CONCEPTS THROUGH
ORGANIC CRYSTALLINE ANALOGS
“WELDING” ORGANIC CRYSTALLINE MATERIALS**

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Abstract

This paper describes the development and use of an organic weld simulator to improve students understanding of epitaxial nucleation, competitive growth, interfacial stability and solidification. The system allows students to directly and synchronously observe solidification at low temperatures. The system takes advantage of the transparency and low melting temperature of several organic compounds to provide students with rare insight into the solidification event, epitaxy, competitive growth and the breakdown of interfacial stability during solidification. Moreover, the apparatus allows the students to manipulate critical process parameters and observe the effects on the solidification process and the inter-phase interface on a real-time basis.

I. Introduction

Solidification processing and other manufacturing processes based on epitaxial nucleation and growth are critical to a number of technologies. Arguably, they support much of the metals industry, underpinning transportation and transport, infrastructure, and many other sectors. In addition, our current communications, electronics and computing industries – the keys to our information age and the basis for our development of the “knowledge” economy of the 21st century rely on epitaxial processing. Clearly, from ships to chips, our economy relies on an ability to manipulate process parameters to produce desirable structures at inter-phase interfaces – in large welds or in minute electronic or electro – mechanical systems.

The study of nucleation, growth and interfacial stability often lacks immediacy. Akin to the lonely paleontologist, students of materials scan the "fossil" remains of long-past-solidified weld pools to gain clues about the nature of the solidification event. Similarly, akin to the forensic pathologist, students of chemical vapor deposition (CVD) or molecular beam epitaxy (MBE) attempt to understand these processes by examining inert pieces of prefabricated and vivisectioned samples.

II. Theory

Melting and solidification are two of the most important reactions involved in fusion welding. In a sense they may be regarded as competing processes which occur simultaneously, each at its own characteristic rate. Thus, at the melting temperature of a pure metal, both solid and liquid may coexist in equilibrium with one another, and one can say that the rates of melting and solidification are equal. If we cool the pure metal to slightly below its melting temperature, the rate of solidification becomes dominant, and the rate of growth of the solid phase is controlled by the rate at which the latent heat liberated can be conducted to the surroundings. Thus, one can say that the control of melting and solidification of a pure metal is strictly a heat flow problem.

Most metals of commercial importance are alloys and, as such, impose an additional constraint on the melting and solidification processes. Except for eutectics and the comparatively rare congruent-melting alloys which exhibit discrete melting points, alloys exhibit a melting temperature range. In general, the composition of the solid and liquid phases in equilibrium with each other are a function of temperature within the melting temperature range. Thus, in addition to the necessity of dissipating the latent heat of fusion, solidification of an alloy involves the redistribution of solute as well. Therefore, the solidification of an alloy involves both heat transfer and mass transfer, and it is important to understand their roles in the solidification of a fusion weld.

Solidification Mechanics

In the production of a fusion weld, a molten weld pool is established and, through control of the process variables, is made to travel at a constant rate without significantly changing its shape. Figure 1 is a schematic representation of an elliptical weld pool with a bounding surface defined by locus of the liquidus temperature of the alloy. Surrounding the weld pool in figure 1 is a dashed curve corresponding to the locus of the effective solidus of the alloy – which is always lower than the nominal solidus expected for any given composition. The volume of the molten phase present varies in a continuous fashion from 0 at the dashed line to 100% at the solid line bounding the weld pool. Unfortunately, the existence and practical significance of this region, called the *partially melted zone*, is not widely recognized.

Assume that the weld pool shown in Figure 1 is created by a heat source located at 0 and moving from right to left with a velocity, V . In an autogenous bead-on-plate weld, melting will be occurring along the leading edge, ABC, of the weld pool. This requires that the latent heat of fusion be supplied to convert the solid to a liquid at the liquidus temperature. At the trailing surface of the weld pool, CDEA, the latent heat of fusion must be liberated to cause solidification to occur. On the average, the growth of the solid occurs parallel to the maximum temperature gradient, which is perpendicular to the advancing solid-liquid interface, CDEA.

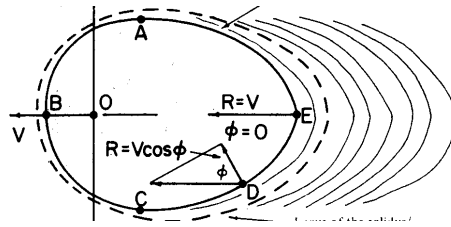


Figure 1. Schematic of a moving pool.

This means that if the shape of the weld pool remains constant, the growth rate of the solid must be given by:

$$R = V \cos \phi \quad (\text{Eq. 1})$$

Where, R = growth rate of the solid at a given point on the moving solid-liquid interface, V = welding velocity and ϕ = angle between the normal to the interface at the particular point (in other words, the average growth direction) and the welding velocity vector. Thus, the growth velocity would vary from $R = 0$ at the sides of the pool (Points A and C) where $\phi = 90$, to a maximum of $R = V$ at the centerline of the weld (Point E) where $\phi = 0$.

Since the rate of liberation of latent heat is directly proportional to the rate of growth of the solid, the rate of heat liberation is maximized at the weld centerline. Unfortunately, the minimum temperature gradient, and therefore the minimum capability to conduct the latent heat to the cooler surroundings, is found at this location. Consequently, when welding velocity reaches a critical value, V_c , such that the rate of growth parallel to the welding direction can no longer be sustained, the weld pool will assume a teardrop shape. Note that, when the pool assumes a teardrop shape, the minimum value of ϕ is increased, and therefore, since $R = V \cos \phi$, the maximum growth rate is reduced. As the velocity is further increased above V_c , the minimum value of ϕ also increases in order to balance the maximum rate of liberation of latent heat with the rate of conduction of this heat to the surroundings.

The volume of the weld pool is directly proportional to the welding current and inversely proportional to the welding velocity. Therefore, increasing the welding current at constant velocity increases the volume of the weld pool without greatly altering its shape. On the other hand, increasing the welding velocity at constant current both decreases the volume of the pool and increases the ratio of its length to its width. The critical velocity at which the pool assumes a teardrop shape is inversely proportional to the welding current.

Epitaxial Growth

In a properly made fusion weld, the base metal is wet by the molten metal in the weld pool and, being similar in composition, acts as an ideal substrate upon which growth of the solid phase can occur. Thus, to extend the solid phase, atoms from the liquid merely surrender their latent heat of fusion to the surroundings and occupy positions corresponding to lattice sites in an extension of the crystal structure of the existing solid. All grain boundaries are continuous across the boundaries of the fusion zone. During solidification, atoms from the liquid liberated their latent

heat of fusion to join and extend the crystal structure of the individual grains along the moving solid-liquid interface. The continuity of the orientation lustre and the complete absence of grain boundaries parallel to the boundaries of the fusion zone provide visual evidence in support of this growth mechanism, known as epitaxial growth. Investigators have conclusively proven that growth is indeed epitaxial with the aid of microbeam x-ray diffraction techniques.

Competitive Growth

The shape of the grains in the fusion zone is controlled by the shape of the weld pool through the action of a phenomenon known as competitive growth. As noted earlier, the average growth direction during solidification of a fusion weld is approximately perpendicular to the solid-liquid surface at all points in the weld pool. However, the growth of each individual grain tends to occur parallel to a particular crystallographic direction, called the *easy growth direction*. In cubic metals, this is a $\langle 100 \rangle$, or cube-edge direction. In hexagonal-close-packed metals, it is the $\langle 1010 \rangle$ direction, which corresponds to the close packed direction in the basal plane. Because of this phenomenon, the shape of the weld pool has an important influence on the shape of the grains in the fusion zone.

Since growth is epitaxial, certain grains growing out of the partially melted region across the fusion boundary will have their easy growth direction parallel, or nearly parallel, to the maximum temperature gradient. Such favorable orientation gives these grains a competitive advantage over adjacent, less favorably oriented grains, in the region just inside the fusion boundary. In the case of an elliptical weld pool, the temperature gradient changes continuously from normal to the welding direction at the fusion boundary to parallel to the welding direction at the weld centerline. Thus, with an elliptical weld pool, the grains tend to curve in the direction of welding as they follow the moving solid-liquid interface, and the competitive advantage shifts from grain to grain as the continual reorientation of the maximum temperature favors differing crystallographic orientations. Note also that each grain in an elliptical shaped pool tends to maintain contact with the moving solid-liquid interface until it is pinched off in a random fashion by neighboring grains.

On the other hand, within a teardrop shaped pool the orientation of the maximum temperature gradient is invariant over a significant portion of the trailing edge of the weld pool. Consequently, when a grain which has a favorably oriented easy-growth direction encounters this region where the orientation of the maximum temperature gradient no longer changes, the favorably oriented grain crowds out its less favorably oriented neighbors. Thus, only grains whose easy growth directions parallel the direction of the invariant maximum gradient survive the competitive growth process. This causes impingement of favorably oriented grains from opposite sides of the weld pool along the center of the weld. A teardrop shaped pool tends to produce a high degree of preferred orientation in the weld. Such a texture could, in some instances, cause dangerous directional differences in the mechanical properties of the weld.

Interface Stability

Commercial solidification processes are never equilibrium in nature, since the transformation from

liquid to solid occurs in finite time. Thus, the interpretation of the solidification process through the phase diagram must be modified to account for the kinetics of the diffusional processes involved. Scheil made an initial attempt, modifying the mass balances inherent in the lever law by assuming that no diffusion occurred in the solid state once a solid had been formed. He also assumed that mechanical mixing in the remaining liquid would be complete, that the solid interface was planar and that at any given temperature, and that the composition of the solid forming from the liquid would be as dictated by the phase diagram. This approach was refined by Tiller, who used all of the assumptions of Scheil, save for that of complete mixing of the solute in the liquid. Because of this last refinement, a processing parameter, R , the growth rate, appears in the equations for the composition found in the liquid as a function of distance from the solid-liquid interface. This approach leads to the modeling of the composition of the liquid near the interface as a transient region in which the liquid composition falls from C_0/k to C_0 over five characteristic distances from the interface- the characteristic distance is given by the expression $5D_l/R$, where C_0 is the nominal composition of the material, k is the equilibrium distribution coefficient, and D_l is the diffusion rate in the liquid. The major difference between the two approaches is that in Tiller's model, the majority of the solid forms in a steady state stage, and is of nominal composition. In Scheil's model, the solid composition varies continuously because no steady state is reached. Both predict the same invariant composition at the end of solidification.

The value of Tiller's contribution is in its establishing the existence of a solute field in the liquid ahead of the solid – liquid interface. This development led directly to the discovery of the phenomenon of constitutional supercooling, and an understanding of the breakdown of the planar solidification interface which leads to different solidification morphologies. Chalmers first recognized this, and combined an expression for the solute concentration ahead of the interface with one for the phase diagram liquidus curve to generate a relation between the “effective liquidus” and position. The result showed that the liquidus temperature reaches a minimum at the solid-liquid interface and rises to a maximum at the end of the solute spike. Depending on the actual temperature distribution in the liquid, a region of “constitutional supercooling” can extend into the liquid, and chance protuberances at the interface can grow into this region. Depending on the extent of this supercooling, different solidification substructures can form, which drastically alter the properties of the solid.

III. The Apparatus

Direct observation of the solid - liquid interface in metals is difficult, metals are not transparent and the temperatures associated with the interface prevent simple observation systems. The interface is a critical region; much of the structure resulting from solidification depends, intimately, on the interface morphology. OWLS allows students to be active participants in the events at the solidification interface, and to observe and alter the structures produced.

Solidification processes depend upon the roughness, on an atomic scale, at the solid-liquid interface. Materials can be classified in terms of their freezing behavior according-to their entropy of melting. Certain organic compounds exhibit entropies of melting that are very similar to those

of metals. The availability of transparent materials for metallic analogs presents an opportunity to directly observe the phenomena that determine the structure of cast metals and fusion welds.

The organic compound found most suitable for purposes of the laboratory was succinonitrile. The specimen was encapsulated in a cell comprised of a slotted brass plate and two rectangular cover glass slides. The cover glasses rested on a lip in the slotted plate. A movable platform held this cell. The platform is comprised of an aluminum plate, slotted to hold the brass cell plate. The plate is mounted on four pillow blocks, that run on case hardened steel rails. The entire platform is driven by a 1/16 horsepower electric motor, providing platform velocities from 4mm to 75mm per minute. Below this assembly, a variable intensity lamp (15 W bulb and rheostat) serves as backlight for viewing. A fixed filament provides heat for this sample. Stainless Steel filament wire (0.1mm) connected to quick release terminals is placed in proximity to the cover glass. The filament is connected to a 2-12V, 0-5 amp power supply. When heated, this filament simulates the welding arc. A stereomicroscope is used to view the "weld pool" region.

This device can be used to view almost all the features associated with welds in metals. Direct observation of epitaxial nucleation, competitive growth, morphological changes in the weld pool and the solidification substructure - even observation of defect formation is possible. Furthermore, the interrelation between macroscopic processing parameters (G, R - as controlled by heat input and travel speed) and microstructure can be observed with this device. The relationship between processing parameters and the macroscopic bead shape can also be clearly observed with this device.

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