

# NOVEL DIRECTIONAL SOLIDIFICATION PROCESSING OF HYPERMONOTECTIC ALLOYS

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## ABSTRACT

Gravity driven separation precludes uniform microstructural development during controlled directional solidification (DS) processing of hypermonotectic alloys. It is well established that liquid/liquid suspensions, in which the respective components are immiscible and have significant density differences, can be established and maintained by utilizing ultrasound. A historical introduction to this work is presented with the intent of establishing the basis for applying the phenomena to promote microstructural uniformity during controlled directional solidification processing of immiscible mixtures. Experimental work based on transparent organics, as well as salt systems, will be presented in view of the processing parameters.

## BACKGROUND

With the intent of producing uniform composites, solidification processing of hypermonotectic alloys in a microgravity environment began with the 1973 Skylab mission and has continued since. In review, the results of later experiments are essentially no different, i.e. extremely disappointing. In microgravity, despite the favorable reduction in acceleration, gravity *independent* factors cause coalescence and massive segregation of the liquid phases. This results in a highly inhomogeneous structure. The proposed work would negate these detrimental factors by utilizing ultrasonic energy to initiate and maintain a uniform dispersion of the excess  $L_{II}$  phase. A thorough experimental and modeling effort will be coordinated with the intent of understanding and optimizing the processing parameters necessary to produce a uniformly aligned hypermonotectic composite during controlled directional solidification. If successful, this technique could be used in conjunction with a low gravity environment to give ideal processing conditions.

The binary miscibility gap system of interest is characterized by 1) a region where two distinctly different liquids are in thermodynamic equilibrium and 2) the monotectic reaction,  $L_I = S_I + L_{II}$ . Note that, although similar in form to the well studied eutectic, one of the reaction product phases is a liquid. Microstructural development at the solid/liquid interface for these alloys has been theoretically discussed by Chadwick<sup>1)</sup> and Cahn<sup>2)</sup> and experimentally investigated by Livingston and Cline<sup>3)</sup> and Grugel and Hellawell<sup>4,5)</sup>.

Alloy compositions to the right of the monotectic reaction are termed hypermonotectic and, upon cooling, pass through the two liquid miscibility gap. Solidification of these alloys for application as, e.g., slide bearings is hampered by the inherent, usually large, density differences between the  $L_I$  and  $L_{II}$  phases. This leads to rapid separation, coalescence and, consequently, a highly inhomogeneous structure. It was envisioned that processing in a microgravity environment would eliminate the density differences and a uniform composite of aligned or finely dispersed  $L_{II}$  (eventually  $S_{II}$ ) in the  $S_I$  matrix could be produced. Unfortunately, microgravity experiments still resulted in highly macrosegregated structures<sup>6)</sup>; ref. 10 lists many papers reporting similar results.

A number of explanations for these poor results have been posed. They include droplet coalescence by Ostwald ripening and/or thermocapillary convection and preferential wetting of the container by one of the liquid phases. These factors, which are both detrimental to microstructure *and* gravity independent, merit consideration.

Earlier experiments where hypermonotectic alloys were directionally solidified<sup>7-9)</sup> served to demonstrate the detrimental effects of phase separation on microstructure. While the above mentioned coarsening and wetting cannot be eliminated, they may be used to some advantage. It has been shown<sup>10-13)</sup> that these gravity independent effects could be accommodated through the inclusion of fibers which served to accrue and uniformly distribute the  $L_{II}$ . As the directional solidification front advances the fibers and adhering  $L_{II}$  are uniformly incorporated into the  $S_I + L_{II}$  matrix. This process, however, does necessitate fibers.

To this end it is suggested to apply an ultrasonic field to the bulk liquid which, upon cooling, will initiate and maintain a uniform dispersion of the precipitated liquid,  $L_{II}$ . The microgravity environment would then serve to eliminate density differences, i.e., settling, between the liquids. With droplet coalescence minimized, controlled directional solidification should promote a uniformly aligned, composite microstructure.

The study of acoustic waves on initiating and maintaining suspensions in two-liquid systems is well established. In 1927 Wood and Loomis<sup>14)</sup> reported using high-frequency sound-waves of great intensity to form emulsions. Shortly after, Richards<sup>15)</sup> used lower intensities of sound and was able to emulsify many liquid immiscibility systems. Mechanisms for emulsification by ultrasonic waves were further investigated in a series of papers published in the 1930's by Sollner, *et al.*<sup>16)</sup> and they were able, using energies of 100mA and more, to emulsify a maximum of 6g mercury in 1 liter of water. Schmid *et al.*<sup>17)</sup> (late 1930's) applied ultrasonics to a number of pure metal and alloy melts. Overall, upon solidification, a comparatively much finer microstructure resulted. They also produced a dispersion of lead in the immiscible aluminum-lead system that was considerably finer at the top. A number of papers reporting the results of applying ultrasonic energy to solidifying melts have since been published [e.g. 18-26]; again overall finer and more uniform microstructures resulted.

Clancy *et al.*, realizing the need for a uniform distribution of droplets and/or particles prior to solidification processing in a microgravity environment, developed an ultrasonic mixing system for use with existing Spacelab furnace hardware<sup>27)</sup>. Subsequently, microstructural examination of a hypermonotectic zinc - 5 wt pct lead alloy, (microgravity environment provided by TEXUS sounding rockets) showed a better distribution of the Pb-phase with acoustics applied than without<sup>28,29)</sup>. In a similar microgravity experiment, Takahashi *et al.*<sup>30)</sup> solidified hypermonotectic aluminum - 30 wt pct indium alloys subjected to ultrasonic energy; again considerably better dispersions were found.

The above experiments examined metallic, miscibility gap systems from which microstructural development must be inferred after solidification is complete. This hindrance may be circumvented by using transparent materials which simulate solidification phenomena in metals and alloys, a well established technique<sup>31)</sup>.

## EXPERIMENTAL ASPECTS

With reference to the succinonitrile - glycerol phase diagram, Fig. 1, consider the following demonstration<sup>32)</sup>.

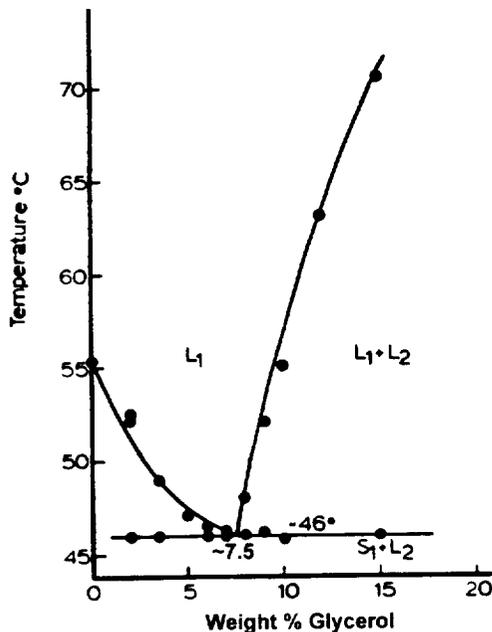


Fig. 1 Partial Succinonitrile - Glycerol phase diagram<sup>33)</sup>.

Hypermonotectic succinonitrile - 15 wt pct glycerol "alloys" were made and placed in 12mm I.D test tubes. The samples were instrumented with a thermocouple and submerged in the water bath of a commercial ultrasonic cleaner, the initial bath temperature being  $\sim 90^{\circ}\text{C}$ . When the bath, and sample, cooled to  $\sim 73^{\circ}\text{C}$  precipitation of the excess  $L_{II}$  phase (glycerol) initiates. After 45 minutes,  $\sim 51^{\circ}\text{C}$ , the coalesced glycerol fully occupies the sample bottom, Figure 2 - left. Subsequent solidification results in a

highly segregated structure. The right side of Fig. 2 shows a similar sample which was subjected to ultrasonic energy during cooling.

At  $\sim 50^{\circ}\text{C}$  and 105 minutes, after precipitation of the  $L_{II}$  phase initiated, a uniform dispersion of the excess liquid is maintained.

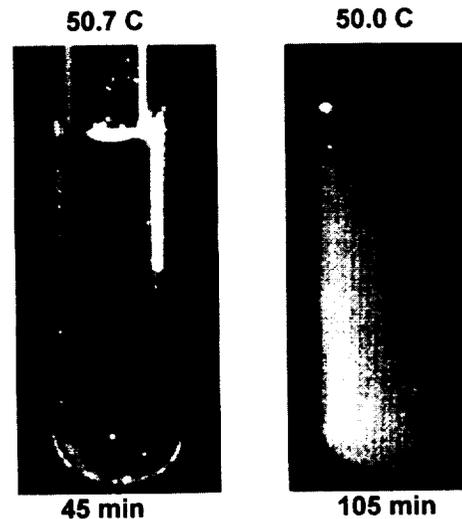


Fig. 2 Left: Settling and coalescence of  $L_{II}$  (glycerol) as the sample cools through the miscibility gap. Right:  $L_{II}$  droplets remain suspended in an ultrasonic field.

Controlled directional solidification experiments generally consider four processing parameters, i.e., growth rate ( $V$ ), temperature gradient ( $G$ ), composition ( $C_0$ ), and gravity ( $g$ ). Applying ultrasonics introduces many additional variables. These include frequency, amplitude, sample dimensions, heat generation, and melt-probe interactions and must be considered. For example, the effect of amplitude is demonstrated in Figure 3. Here a given amount of tin was melted in a zinc chloride - sodium chloride flux after which ultrasonic energy (20 kHz) was introduced for  $\sim 1$  minute. In Figure 3a the amplitude was  $64\mu\text{m}$ , in Figure 3b the amplitude was  $137\mu\text{m}$ ; an obviously finer droplet dispersion is observed as a consequence of the higher amplitude.



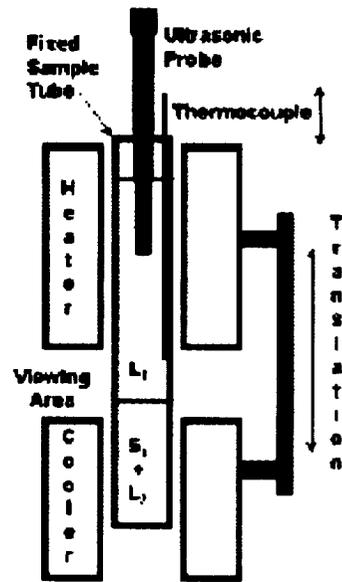
(a)



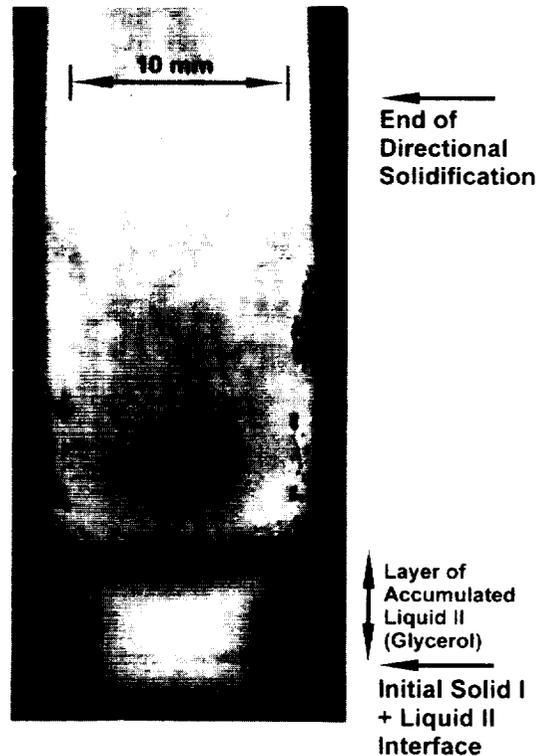
(b)

**Fig. 3** Tin droplet dispersions as a consequence of applying ultrasonic ( $f = 20$  kHz) energy with a probe amplitude of (a)  $64\mu\text{m}$  and (b)  $137\mu\text{m}$  for  $\sim 1$  minute.

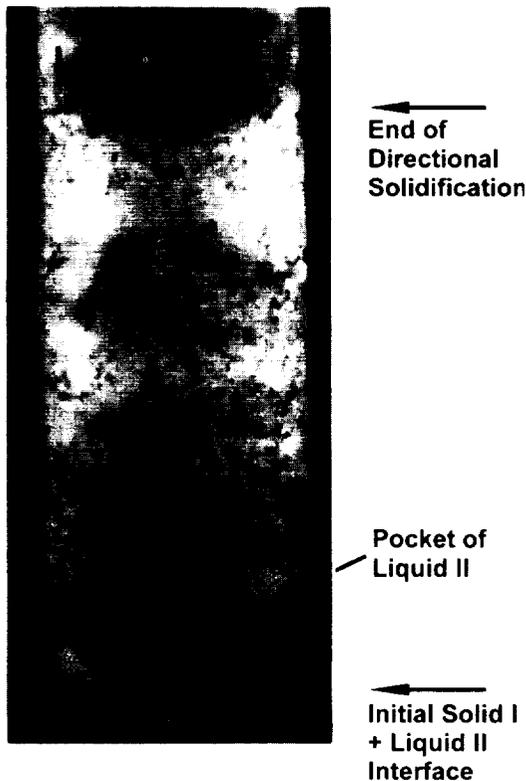
A schematic representation of the directional solidification apparatus used in this investigation is depicted in Figure 4. Here the sample and probe are fixed with the heating-cooling units translated at the desired rate. The heater consists of a resistance winding ( $\sim 1\text{cm}$  intervals) around a quartz tube which permits direct observation and recording of events at the solid/liquid interface.



**Fig. 4** Schematic representation of the directional solidification apparatus used in this investigation.



**Fig. 5a** Macrograph of a Succinonitrile - 15 wt pct Glycerol "alloy" directionally solidified at  $5\mu\text{m}\cdot\text{s}^{-1}$ . The layer of Liquid<sub>II</sub> (glycerol) forms during melting prior to reaching equilibrium. Note that the sample tube is 12mm OD, 10mm ID.



**Fig. 5b** Improved microstructural uniformity as a consequence of applying ultrasonic ( $f = 20$  kHz) energy with a probe amplitude of  $137\mu\text{m}$  for 0.1 second/second during controlled directional solidification.

The macrostructure of a hypermonotectic “alloy” which has been directionally solidified in the above mentioned furnace is shown in Figure 5a. Clearly visible is a layer of excess, denser,  $L_{II}$  that has accumulated at the (now) equilibrium  $S_I + L_{II}$  interface as established by the temperature gradient. From observation, the layer of glycerol initially forms once the sample is placed into the furnace. Initially, as it heats up, the mixture passes through the two liquid region prior to reaching an equilibrium  $L_I$  temperature. During this time precipitated  $L_{II}$  can sink and accumulate; if heating was instantaneous this would be minimized. Secondly, it takes time for the  $S_I + L_{II}$  interface to stabilize. As it slowly melts back and passes through the miscibility gap the denser glycerol contributes to the  $L_{II}$  layer. Conversely, the less dense succinonitrile-rich  $L_I$  develops under the  $L_{II}$  layer until a sufficient

mass is developed which then releases, passes through the layer, and contributes to the upper bulk liquid. Obviously, the desired microstructural homogeneity is compromised by this process.

In contrast, Figure 5b shows an identical sample that was directionally solidified in the presence of an applied ultrasonic field. Here only a small pocket of  $L_{II}$  accumulated at the  $S_I + L_{II}$  interface. The horizontal banding is a result of manually moving the probe tip in relation to the advancing interface. It is envisioned that the  $L_{II}$  pocket can be further minimized (or eliminated) by optimizing the processing parameters. Banding will be controlled by modifying the experimental apparatus such that the probe moves in conjunction with the heating and cooling units. Further work involves scaling and applying the processing parameters to a metallic sample from which microstructural and compositional analysis will be facilitated.

## SUMMARY

A review of the literature and some initial experiments have illustrated that ultrasonic energy can promote and maintain finer and more uniform dispersions during solidification processing of immiscible alloy systems. Directional solidification experiments of transparent materials demonstrated sedimentation, a consideration that is minimized by introducing ultrasonic energy. Processing in a microgravity environment will minimize sedimentation, but not coalescence, during melting and subsequent solidification; this makes a case for including ultrasonic capabilities. Furthermore, we might expect the microgravity environment to extend the volume fraction of a suspended dispersion as well as provide benchmark samples to which mathematical models and Earth-processed samples can be unequivocally compared.

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