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SEPARATION PROCESSES DURING BINARY MONOTECTIC ALLOY PRODUCTION

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16. Abstract

Generally, attempts to solidify immiscible mixtures to make binary alloys, in-situ, yield poorly dispersed composites. By and large, the situation is more pronounced for hypermonotectic compositions than for either monotectic or hypomonotectic solutions. There is considerable interest among metallurgists to understand processes causing liquid-liquid and solid-liquid phase separations during monotectic alloy solidification. Knowledge of such dynamics must precede accurate predictability of the behaviors of solidifying metallic systems and control of their microstructures.

If a homogeneous melt is cooled into an immiscible region, the newly formed second phase will generally have a density different from the parent phase, and will separate readily by sedimentation. Observation of microgravity solidification processes indicates that outside of sedimentation, at least two other important effects can separate the phases; (1) critical-point wetting and spreading, and (2) thermal migration of second-phase droplets due to interfacial tension gradients. It is difficult to study these surface tension effects while in a unit gravity field. Considerable work has been done using neutrally buoyant systems, but such systems are generally neutrally buoyant only at one temperature. Therefore, in order to investigate the processes occurring over a temperature range, i.e., between a consolute point and the monotectic temperature, it is necessary to use a low-gravity environment. The MSFC drop tube (and tower), the ballistic trajectory KC-135 airplane, and the Space Shuttle are ideal facilities to aid formation and testing of hypotheses.

Much of the early work in this area focuses on transparent materials so that process dynamics may be studied by optical techniques such as photography for viewing macro-processes; holography for studying diffusional growth, spinodal decomposition and coalescence; ellipsometry for surface wetting and spreading effects; and interferometry and spectroscopy for small-scale spatial resolution of concentration profiles.

Finally, computer models developed from the transparent model studies will be quite helpful when applied to existing metallic specimens already prepared in low gravity. Additional metallic samples solidified in the MSFC drop tower will test the accuracy of predictions based on such studies.

17. Key Words (Suggested by Author(s))

Monotectic Alloys, Miscibility Gap Systems, Critical-Point Wetting, Thermal Migration, Spinodal Decomposition, Nucleation and Growth, Microgravity Experiments, Succinonitrile-Water System, Transparent Models for Metallic Solidification

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I. INTRODUCTION

Monotectic systems are characterized by a region of liquid phase immiscibility. If a melt is cooled into the immiscibility region, the minority phase nucleates and grows by diffusion into fine droplets or separates by spinodal decomposition. Since the two liquid phases virtually always have different densities, the phases rapidly separate by Stokes migration in unit gravity. Unless the system is quenched extremely rapidly, which can only be accomplished on a very small-length scale, phase separation will be virtually complete when the melt solidifies. Therefore, it is not possible to make alloys or finely dispersed in-situ composites with systems having liquid phase miscibility regions by normal casting techniques.

Reger [1] has enumerated some 500 metallic systems that exhibit a liquid phase immiscibility region. Gelles identified some potential uses for such materials if they could be formed. Suggestions included lower-cost, electrical contact materials and materials with unique electrical and superconductive properties [2]. Certainly, such composites can be prepared by various powder metallurgical techniques or other mechanical methods, but there generally is not the same intimate contact between the two phases as can be achieved by forming in-situ composites directly from the melt. Since many of the interesting properties of such systems are thought to depend on this interface, there is an interest in developing techniques for forming these in-situ composites.

It is possible to form in-situ composites at the monotectic and hypomonotectic composition in unit gravity by directional solidification [3]. At the monotectic composition, phase separation does not occur until the host phase solidifies. The solution behaves very much as a low volume fraction eutectic except that the second phase is still liquid. If the system is configured such that it is stable against convection (i.e., liquid second phase is not transported away from the interface by gravity), the second phase will be incorporated into the host phase in the form of spherical droplets or cylindrical columns, depending on the growth rate and interfacial tension relations.

Similar results may also be obtained with hypomonotectic compositions. In this case, pure host material will solidify until the rejected component builds up to the monotectic composition. At this point growth proceeds just as in the case of a monotectic composition except that the lower volume fraction must be compensated for by finer second-phase columns or drops and/or wider spacing between the second-phase material.

In the case of hypermonotectic composition, the excess lower melting liquid is not incorporated into the host phase, but is separated by density differences and possibly capillarity effects. The resulting solid exhibits complete separation between the monotectic and the excess second-phase material.

Since density differences between the two liquid phases provide an obvious gravitationally dependent separation mechanism, it should be possible to virtually eliminate this effect by quenching and solidifying a hypermonotectic system in a low-gravity environment. Lacy and Otto [4] produced fine dispersions of Ga in a Bi matrix by quenching a 50 A% (64 V% Bi) melt in a Ta crucible through the two-phase region during the 4-s free fall provided by the drop tower at MSFC. The finely-dispersed in-situ composite exhibited a much different resistivity versus temperature behavior than the control samples solidified in unit gravity, probably because of the much larger interfacial area associated with the fine dispersion.

II. REVIEW OF MICROGRAVITY EXPERIMENTS

The successful Bi-Ga experiments carried out by Lacy and Otto in the drop tube prompted some larger-scale experiments on rockets and space vehicles. Lacy and Otto investigated the stability of two-phase liquid systems in a demonstration experiment on Skylab [5]. Mixtures of 25, 50, and 75 V% Krytox oil and water in glass tubes were shaken and photographed. While the mixtures separated in tens of seconds on the ground, the space samples remained completely mixed under isothermal conditions for at least 10 hr. This is rather surprising considering the large surface energies involved. Unfortunately, no attempt was made to cool or solidify the mixture.

Lacy and Ang melted and solidified a Zn-20 A% Pb (66.7 V% Zn) sample in a graphite crucible on the Apollo-Soyuz flight [6]. Instead of the expected fine dispersion of Pb particles in a Zn matrix, the sample exhibited almost complete phase separation with two Zn-rich regions surrounded by a Pb-rich region. Smaller Pb globules were found in the Zn-rich region. Whether these were entirely the result of the monotectic reaction, or whether they represented excess Pb, was not determined. The investigators considered that this unexpected behavior might have been caused by incomplete homogenization of the sample. The phase diagram was redetermined [7], and it was found that the consolute point was somewhat higher than the previously accepted value, but was still below the soak temperature used in the flight experiment. If, however, the diffusion coefficient depends on the difference between the soak temperature and the consolute point, the reduced temperature margin may have been such that the 1.6-hr soak time was insufficient to complete diffusive mixing of the sample.

A similar result was obtained by Gelles on the SPAR II rocket flight with two Al-In alloys, 40 wt% In (19.8 V%) and 70 wt% In (46.4 V%), in alumina crucibles [8]. The samples were soaked at 150°C above the consolute temperature for 15 min before launch. The samples were quenched through the two-phase region to a point well below the monotectic point during the 5-min, low-g portion of the rocket flight. Almost complete phase separation was observed with the In-rich phase between the crucible wall and the Al-rich central core. Again, some In globules were found in the Al-rich core, but a quantitative analysis to determine if the Al-rich core was of overall monotectic composition or contained excess In was not reported.

After Lacy and Ang had raised the question of adequate soak time for sample homogenization, this Al-In experiment was repeated on SPAR V, along with 30 wt% In (13.7 V%) and 90 wt% In (76.9 V%) samples. However, this time the sample was soaked for 16 hr above the consolute point before launch. Separate tests were run in which X-ray photographs of the sample in the furnace confirmed that the sample had no detectable phase boundary after a few hours of soak. The results for the three samples in which Al was the majority phase were virtually identical to those of SPAR II [9].

In the 90 wt% In sample, there were two nearly spherical Al-rich regions (one considerably larger than the other) surrounded by In-rich material. The most interesting feature in the microstructure was the presence of a large number of Al-rich spherules in the In surrounding the Al-rich regions. These spheres increase in size as they approach the Al-rich phase. The region containing these Al-rich spherules is, in turn, surrounded by a region that contains virtually no Al spheres but contains Al dendrites. These results eliminated the possibility of phase separation resulting from inadequate mixing and confirmed that there are very significant nongravity forces that cause phase separation in monotectic systems. The success of forming in-situ composites from such systems hinges on understanding and controlling these driving forces.

III. THERMAL MIGRATION

These unexpected results prompted the investigators to take a more serious look at some of the nongravity-related phase separation mechanisms. One mechanism that received considerable attention is droplet migration in a thermal gradient resulting from the fact that surface tension varies with temperature. The first-order theory was developed by Young, Goldstein, and Block (YGB) [10] and predicts that gas bubbles or other fluid second-phase droplets will migrate with a rate that is proportional to the negative of the product of the radius, the derivative of interfacial tension with respect to temperature, and the thermal gradient. If the interfacial tension decreases with increasing temperature, which is the case for most materials, the droplets of the minority phase will migrate in the direction of the thermal gradient.

One of the first experiments at the Marshall Space Flight Center to investigate interfacial tension driven separation processes used a transparent solution to study droplet migration in a thermal gradient. Since only liquid phase effects were of interest in this study and not the solidification reaction itself, the only criteria were that the system form a miscibility gap with a convenient critical temperature, be transparent for easy observation, and have relatively low toxicity. For these reasons, diethylene glycol (DEG) and ethyl silicylate (ES) solutions were appropriate candidates for the investigation. A special test cell provided a vertical temperature gradient with minimal horizontal gradients. Prior to loading the cell, a vessel containing DEG-ES was equilibrated at 20°C (which is below the consolute point). The phases separate with the less dense, DEG-rich phase at the top and the more dense, ES-rich phase at the bottom (Fig. 1). An aliquot of the DEG-rich phase was isothermally transferred to the test cell. A thermal gradient was then established by means of a thermoelectric cooler in the base of the cell and a heater in the top. This causes heavier ES-rich droplets to form in the DEG-rich phase. Under isothermal conditions, the drops would slowly fall, but the imposed thermal gradient was sufficient to cause the droplets to migrate upwards against gravity. The droplets were photographed periodically to obtain their size and velocity (Fig. 2), and their motion was compared to the theoretical result predicted by the YGB model [11].

It should be remembered that the YGB equation is strictly valid only for a stationary drop and does not account for solubility variations with temperature. The experimental test of the theory performed by YGB consisted of balancing the Stokes rise of a bubble in silicone oil against the thermal migration forces from a vertical thermal gradient. Papazian [12] attempted to measure bubble motion in CBr_4 during a SPAR rocket flight, but the bubbles did not move. It was suspected that surface

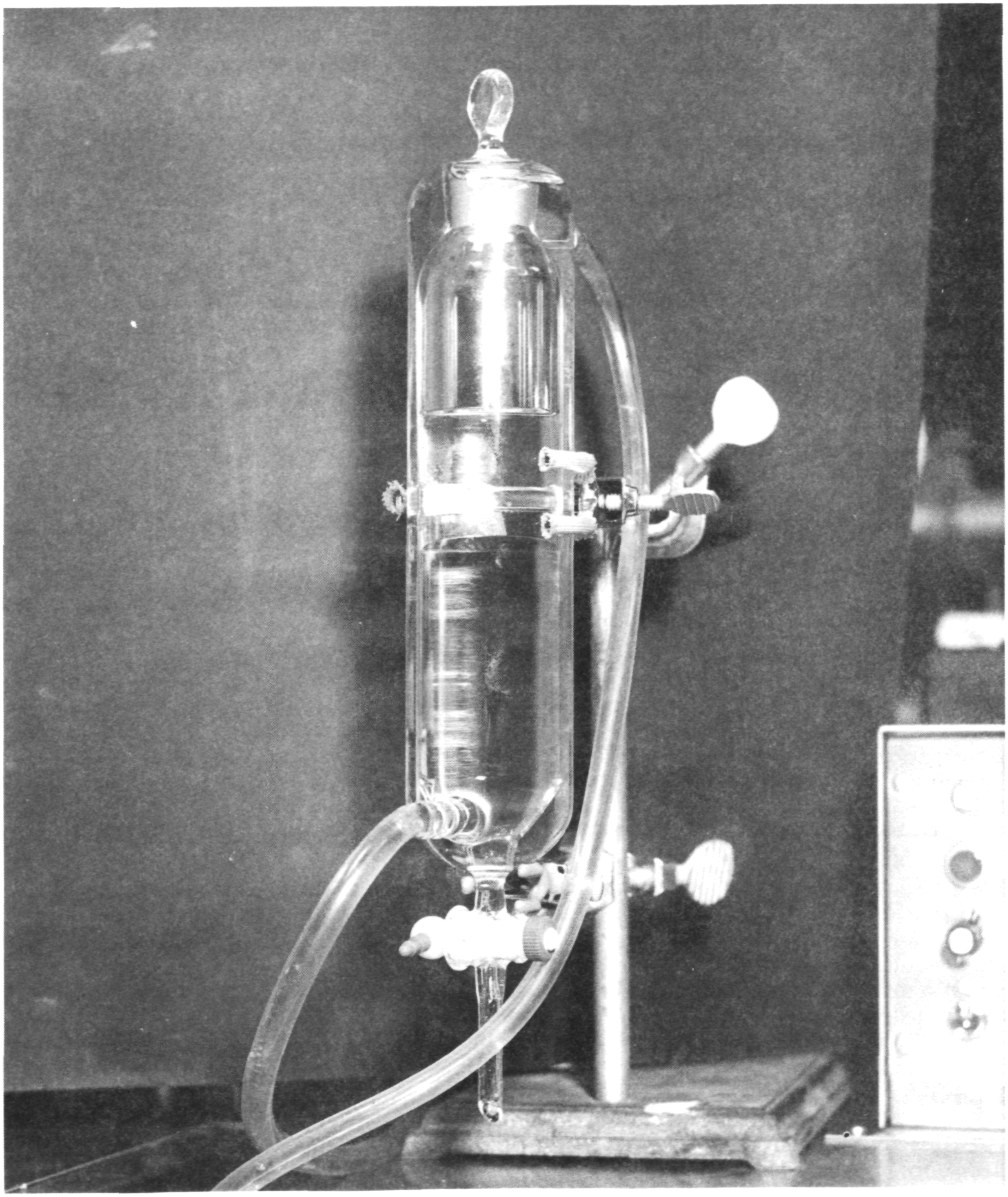


Figure 1. Isothermal phase equilibration chamber.

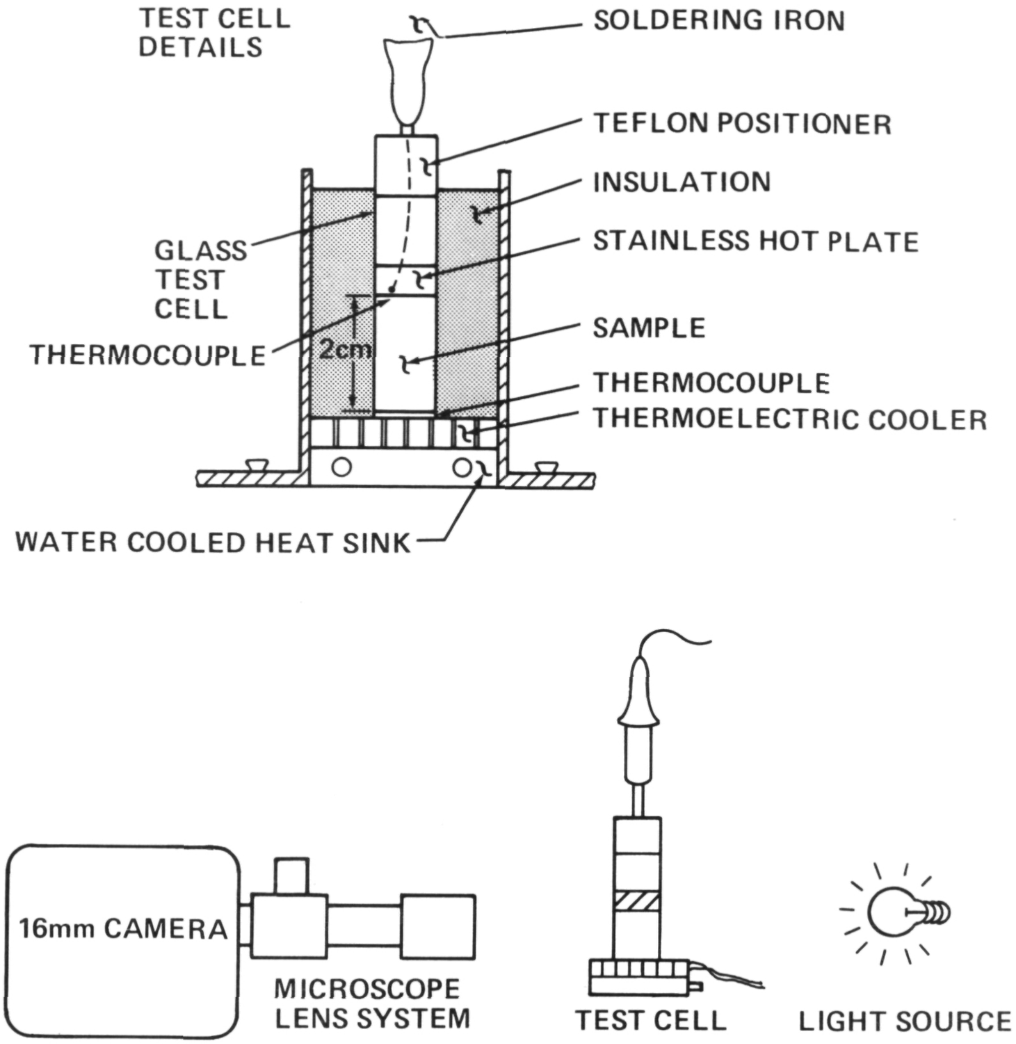


Figure 2. Schematic of immiscible fluid thermal migration apparatus.

active contaminants may have prevented the motion. Thompson et al. [13] were successful in observing thermal migration of bubbles in a drop tower experiment.

The situation is somewhat different in a liquid-liquid system, however, especially when solubility varies appreciably with temperature, and one of the dissolved components may be surface active. The purpose of this measurement was to see how well the YGB theory applied to the two-phase region of a monotectic system.

There was considerable scatter in the data due to the difficulty in measuring the particle diameter and velocity from the photographs, and to uncertainties in the temperature field in the vicinity of the bubble. The difference between measured and theoretical results (after accounting for Stokes settling) was -31.9 ± 13.8 percent. The scatter in the data is large, but it appears that the measured velocities are considerably lower than predicted. One must conclude that there are important effects not accounted for in the YGB analysis.

In spite of apparent deficiency in the theory, qualitative concurrence with experiment suggests that this may have been the mechanism that produced the result observed in Gelles' 90 wt% In sample. However, the other samples solidified in low gravity that showed phase separation had the minority phase surrounding the majority phase, just the opposite of what would be expected from surface-tension-driven droplet migration. Obviously, other effects must predominate in these cases.

IV. CRITICAL-POINT WETTING

Cahn's theory [14] of critical-point wetting predicts that one of the two phases will completely wet the container or the surface as the critical point is approached. If the majority phase wets the container (or the free surface of a containerless drop) in preference to the minority phase, as was the case in Gelles' 90 wt% sample, the liquid is already in a stable configuration, and surface-tension induced droplet migration will possibly be the most significant phase separation mechanism in the absence of gravity-driven effects. On the other hand, if the minority phase preferentially wets the container or outer surface of the drop, the configuration is unstable, since the surface is made up mostly of the majority phase, and the free energy of the system could be reduced considerably by interchanging the minority and majority phases. If a minority phase droplet is on the surface, it will immediately spread over the entire surface. As the material flows to replace the spreading droplet, other droplets find their way to the surface. There is still the competing effect of thermal migration; and, under some circumstances, droplets far from the surface may be driven to the center by surface-tension migration in the direction of the thermal gradient.

Potard [15] reasoned that it should be possible to prevent the massive phase separation observed by Gelles in his low In compositions by choosing a crucible material that was wet preferentially by the Al-rich majority phase rather than by the In-rich minority phase. He flew Al-In samples with 32 wt% In (9.15 V%) and 16 wt% In (monotectic composition) in SiC crucibles on SPAR IX. The ground control monotectic sample was found to be In-rich near the bottom of the crucible. The flight monotectic sample was found to be hypomonotectic near the crucible walls (first to freeze region) and contained some In globules in the interior, indicating that the composition was probably slightly hypomonotectic. The hypermonotectic flight sample did not undergo the massive phase separation observed by Gelles, but instead contained many small In-rich globules ranging in size from 40 to 400 microns with a peak at about 67 microns distributed throughout a matrix of Al monotectic composition. The spatial distribution of the spheres was by no means uniform either, in fact the region around the crucible walls contained no In-rich spheres. Also, In lenses were found on the free Al surface; however, the experiment did provide an important first step in the control of the separation process.

The results of this experiment, and others, causes a significant number of researchers to believe that critical wetting phenomena plays a major role in the phase separation and solidification of a monotectic system. For example, Perepezko [16], using quasi-containerless metal-emulsion techniques, reports that it is possible to undercool some systems with composition on one side of the immiscible region, but not on the other side. The samples that did not undercool were found to be encased in a shell of the minority-phase material, which happened to have a lower interfacial energy in the host fluid. Samples in which the majority phase was the wetting phase did not phase separate, but instead produced more or less uniform dispersions, just as in the flight experiments of Gelles and Potard.

Critical-point wetting occurs in the domain of Young's equation that does not contain real solutions for the contact angle. Young's equation can be written

$$\gamma_{L_1L_2} \cos \theta = \gamma_{L_2S} - \gamma_{L_1S} ,$$

where θ is the contact angle and γ is the interfacial energy corresponding to the interface denoted by the subscript pair. The two liquid phases are denoted by L_1 and L_2, and S is any arbitrary surface which could be a free surface of the two liquids, the solid of one of the two liquids, or an external container. According to Cahn's theory [11] of critical-point wetting, both the liquid-liquid interfacial energy and the difference between the two liquid-solid interfacial energies vanish as the critical temperature is approached and the two liquid phases become a single liquid phase. However, $\gamma_{L_1L_2} \propto (T_c - T)^{1.3}$ and $|\gamma_{L_2S} - \gamma_{L_1S}| \propto (T_c - T)^{0.3}$. Therefore $\gamma_{L_1L_2} < |\gamma_{L_2S} - \gamma_{L_1S}|$ at some temperature T_w before the critical point, and Young's equation does not apply (i.e., $\cos \theta > 1$ is undefined) in the domain $T_w < T < T_c$. This is the region of critical-point wetting in which the fluid phase with the lesser interfacial energy intrudes between the other fluid and the surface. Moldover and Cahn [17] demonstrated this transition by showing that a denser phase (CH_3OH) completely surrounds and overlays a lower-density phase (C_6H_{12}).

Critical-point wetting has two significant implications to the solidification of monotectic systems. First, as discussed, if the minority phase wets the container in preference to the majority phase, phase separation can occur as the temperature is lowered with the two-phase region by capillarity as the minority phase spreads along the container wall. This can essentially be avoided by choosing the container such that the majority phase is the wetting phase. The second implication is that as the primary solid, S_1, begins to form at the monotectic temperature it will be preferentially wetted by liquid L_1. If $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$, perfect wetting occurs, and a film of L_1 intrudes between S_1 and L_2. As the temperature is reduced below the critical point, $\gamma_{L_1L_2}$ increases more rapidly than $\gamma_{S_1L_2}$, and the above inequality reverses at the critical wetting temperature T_w. If this critical wetting temperature is higher than the monotectic temperature, critical wetting does not occur, and a stable three-phase junction can form at the growth front which allows steady-state composite growth. This is typical of systems with a large difference between the consolute and monotectic temperatures, e.g., Al-In. On the other hand, if the critical wetting temperature is below the monotectic temperature, the L_1 phase will intrude between the advancing solidification front and the L_2 phase, and will tend to push the L_2 phase ahead of the front with a force determined by the disjoining pressure. When the other forces on the droplet (drag plus gravitational) are sufficient to overcome the disjoining pressure, the droplet is engulfed by the advancing front [3,18]. This accounts for the globular distribution of second-phase material in systems having a smaller temperature difference between the critical point and the monotectic temperature; e.g., Cu-Pb.

Succinonitrile-H_2O (SN-H_2O) solutions are thought to be in this second category. These solutions are ideally suited as monotectic alloy model materials. Aside from being transparent, having a miscibility gap and relatively low toxicity, these solutions contain succinonitrile, a "plastic" crystal with a low entropy of fusion and are suitable as solidification analogs for metals. Though succinonitrile-H_2O may be in the category [3] in which T_w is below the monotectic temperature, accurate determination of its T_w has not been made. Provided its $T_w < T_m$, SN-H_2O could serve as a good model for some metallic solutions, but another model must be found to represent the systems that have stable three-phase junctions. Aside from at least one component being an appropriate model, requirements are that the solutions have large differences between the critical point and the monotectic temperature and still be in a convenient temperature range for visual analysis at ambient conditions.

It now becomes necessary to devise techniques for measuring the critical wetting temperature for a given surface. One technique, although indirect, is to measure the parameters $\gamma_{L_1L_2}$, $\gamma_{L_1S_2}$, and $\gamma_{L_1S_2}$ as functions of temperature and extrapolate to determine the temperature T_w at which $\gamma_{S_1L_2} = \gamma_{S_1L_1} + \gamma_{L_1L_2}$. The $\gamma_{L_1L_2}$ can be measured directly by passing a DuNouy ring through the interface of L_1 and L_2 and measuring the interfacial tension directly with a Cahn electrobalance. The γ_{SL_1} and γ_{SL_2} are somewhat more difficult. One possibility is to measure the heat of immersion as a clean surface, S is lowered into L_1 or L_2. The heat released q_{imm} is related to the Gibbs [19] energy per unit interface γ_{SL} by

$$q_{imm} = \gamma_{SL} + TS = \gamma_{SL} - T\,\frac{\partial \gamma_{SL}}{\partial T} \quad .$$

However, q_{imm} is usually small and is difficult to measure precisely. An alternative is to measure adsorption isotherms for the surface in question using ellipsometric techniques to obtain film thickness. Once this thickness X on surface S is determined as a function of pressure P of the vapor from L_1 or L_2 at a given temperature T, the film pressure, $\pi°$, is given by combining the Gibbs [19] equation with the ideal gas approximation,

$$\pi° = \gamma_S - \gamma_{SV}° = \frac{RT}{V°} \int_0^{P°} X(P)\, d\ln P \quad ,$$

where γ_S is the surface energy of the solid and V° is the molar volume adsorbed under standard conditions. By carrying out the integration to P°, the saturated vapor pressure, the difference $\gamma_S - \gamma_{SL}$ may be obtained. By repeating the process for the other phase liquid and subtracting the resulting film pressures, the surface tension of the solid is eliminated, and the desired quantity $\gamma_{L_1S} - \gamma_{L_2S}$ is obtained. From this and measured values of $\gamma_{L_1L_2}$, the contact angle is calculated from Young's equation. The entire process must be repeated at different temperatures and the results extrapolated to find the critical wetting temperature at which point $\gamma_{L_1L_2} = |\gamma_{L_2S} - \gamma_{L_1S}|$.

A more direct approach is simply to measure the contact angle by observing the two liquid phases in contact with the solid. The primary difficulty with this approach is that the interfacial tension between the phases gets vanishingly small as T approaches the critical point. Since the two liquid phases generally have a significant density difference, the gravity force on the two liquids is much larger than the interfacial tension, and the phase boundary becomes very flat. The contact angle appears to be 90°, when in reality, it is approaching 0°. The extremely small radius of curvature of the interface near the surface, together with optical distortions from the front and rear surface of the cuvette, makes it extremely difficult to obtain precision measurements of the contact angle. This situation can be alleviated by making the measurement in low-g, where the shape of the interface is dominated by interfacial tension rather than gravity (Fig. 3). Since the adjustment of the interface from 1-g to 0-g should be quite rapid, this measurement should be possible by simply photographing the interface of a thermostated cuvette containing L_1 and L_2 during the free fall time in a drop tower and KC-135 aircraft flying a ballistic trajectory.

In addition, the dynamics of the liquid speading on a surface due to critical-point wetting is important. It is possible to measure the rate of growth of such a film by ellipsometry. Compositions in which the nonwetting phase is the majority phase are considered unstable with respect to critical-point wetting. Equalized phase densities (by D_2O addition) permit film growth measurement after cooling slowly into the two-phase region.

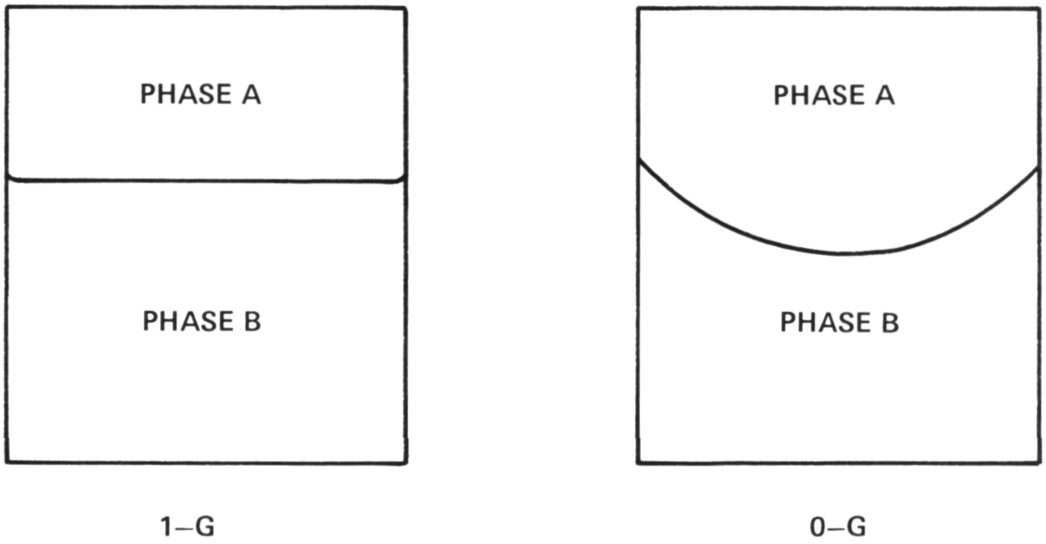


Figure 3. Expected behavior of two-fluid/solid interface near the critical-wetting point in normal gravity and in low-gravity. As the interfacial tension between the two fluids becomes small the contact angle approaches zero. In the 1-g case, hydrostatic pressure flattens the interface making small contact angles difficult to measure. In 0-g, this pressure is removed and the interface shape is determined solely by interfacial effects. Now small contact angles can be easily measured.

V. NUCLEATION AND GROWTH STUDIES

A major difficulty in studying metallic monotectic systems is that most of the information must be gleaned from the final solidified product. It is, therefore, not possible to examine the path or the details of the phase separation process, or even to distinguish between separation processes taking place in the fluid and those involved in the solidification. For these reasons, considerable effort over the past several years has been devoted by workers in the Space Processing Division at the Marshall Space Flight Center in developing and characterizing various transparent analog systems for studying the various phase separation mechanisms.

DEG/ES solutions were highly purified and thoroughly characterized in terms of density, index of refraction, surface tension, interfacial tension, phase diagram, and activity coefficients [20,1]. Nucleation and growth studies were conducted by carefully cooling into the two-phase region in a test cell (Fig. 4) immersed in a temperature-controlled water bath (Fig. 5). By restricting the thickness of the cell to 100 microns, the material remained optically thin during nucleation and initial growth of the second phase droplets. This allowed the use of holography to record the expected particle densities (10^7 particles/cm^3; Fig. 6) during droplet growth and migration.

Holograms taken at various intervals simultaneously recorded the droplets throughout the entire volume of the test cell at specific times. These were later reconstructed and analyzed at an apparent magnification of 1200X (Figs. 7 and 8). Droplets as small as 3 microns in diameter can be resolved, accurately sized, and counted, using an automated video analyzer (Bausch & Lomb Omnicon System; Fig 9). By following the evolution of the distribution of particle sizes with time, growth rates are established. As may be seen in Figures 10a through 10c the number of particles

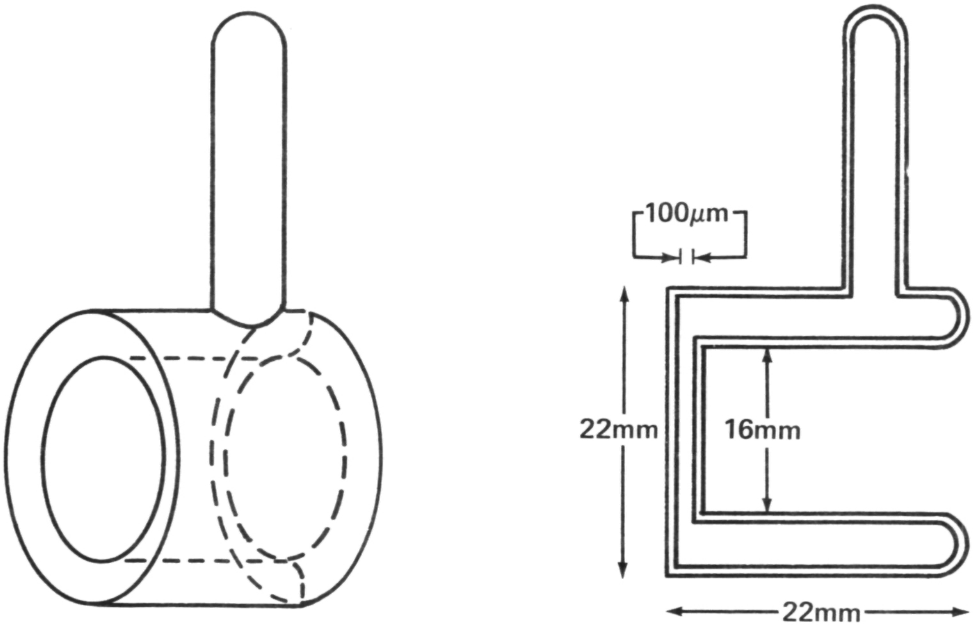


Figure 4. Test cell.

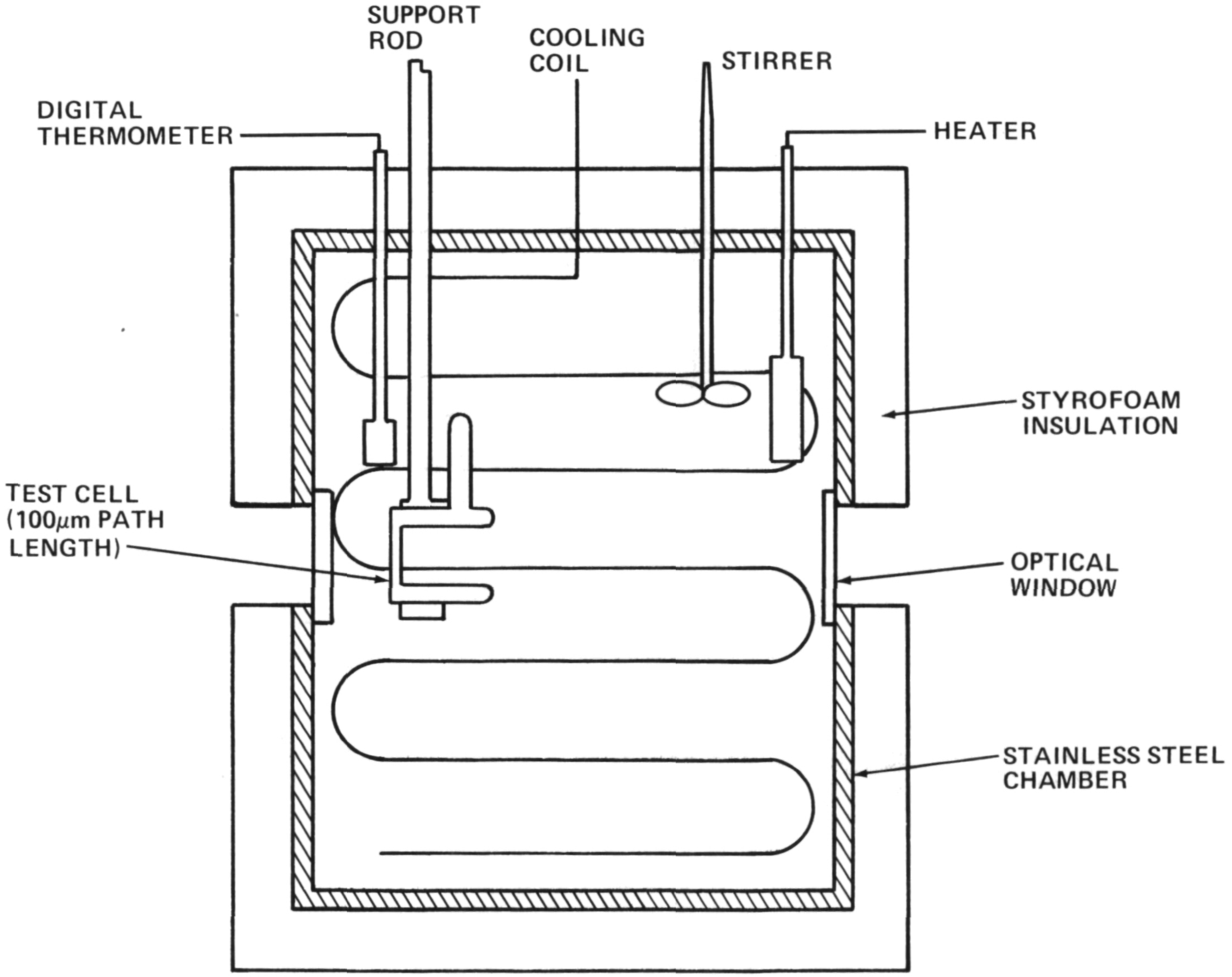


Figure 5. Holographic isothermal test chamber.

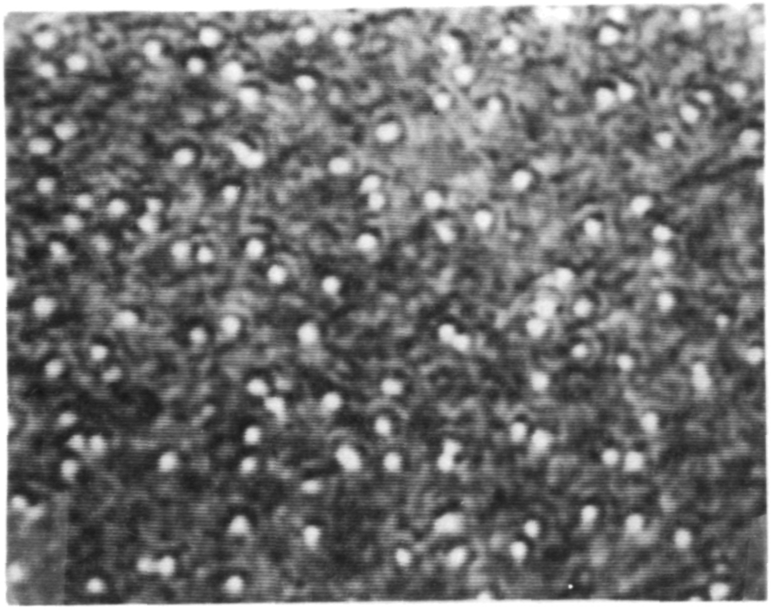


Figure 6. 10^7 particles/cm^3 in a 100 μm path length test cell.

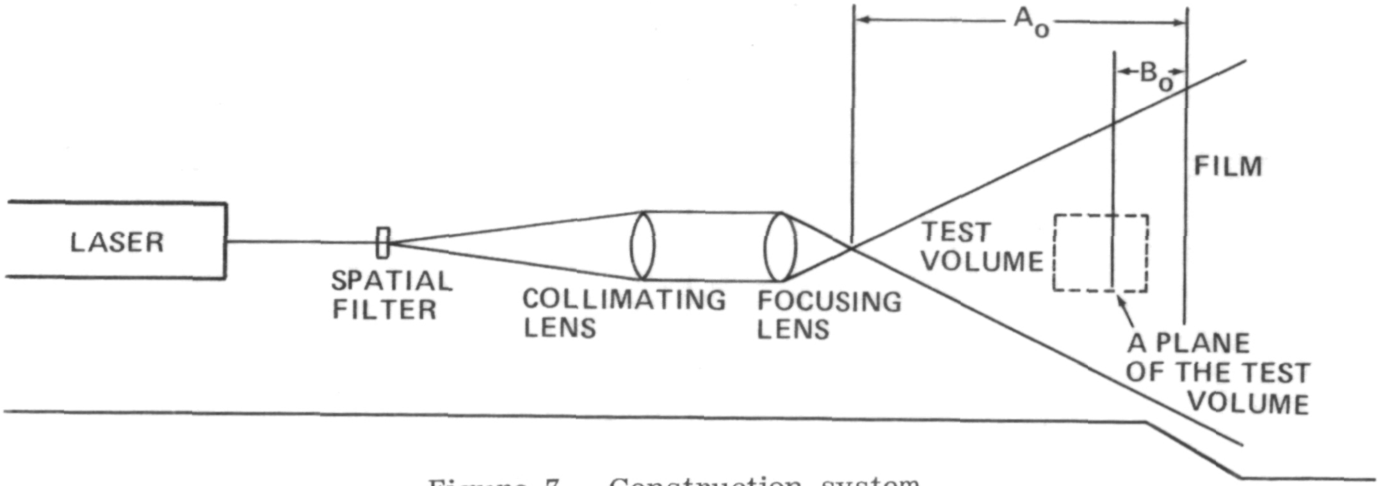


Figure 7. Construction system.

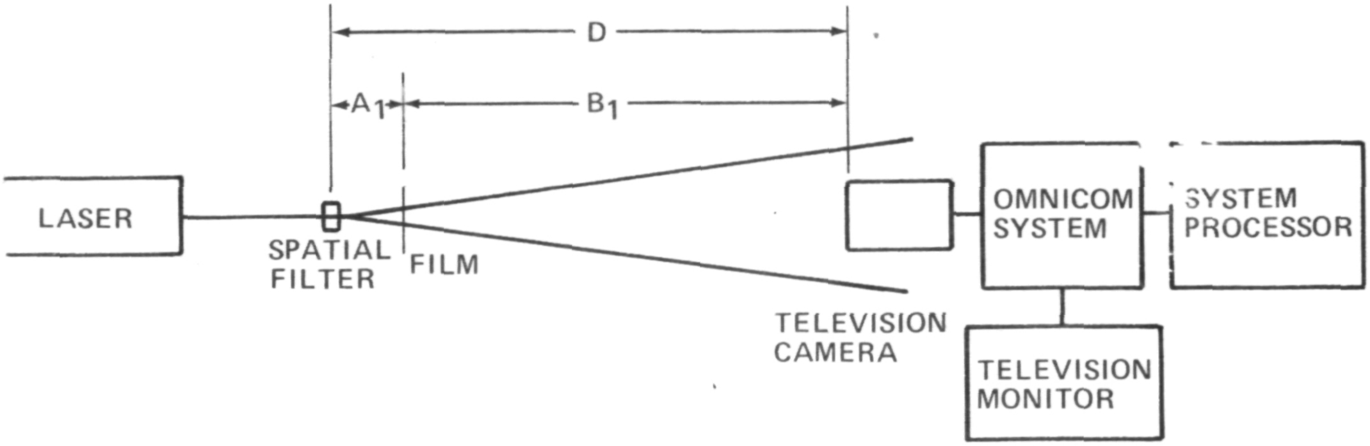


Figure 8. Reconstruction system.

Figure 9. Bausch and Lomb automated feature analysis Omnicon system.

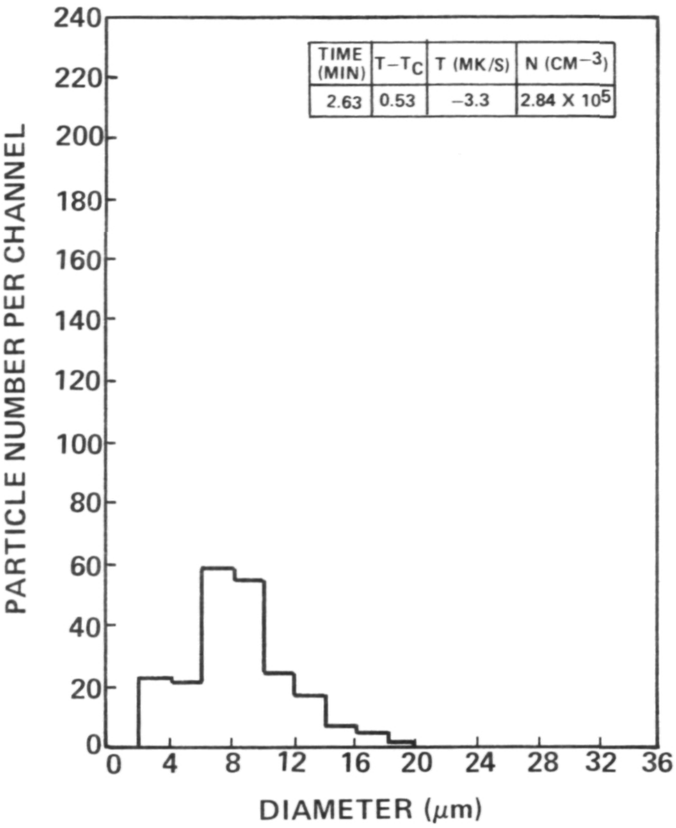


Figure 10a. Particle size distribution, hologram No. 114.

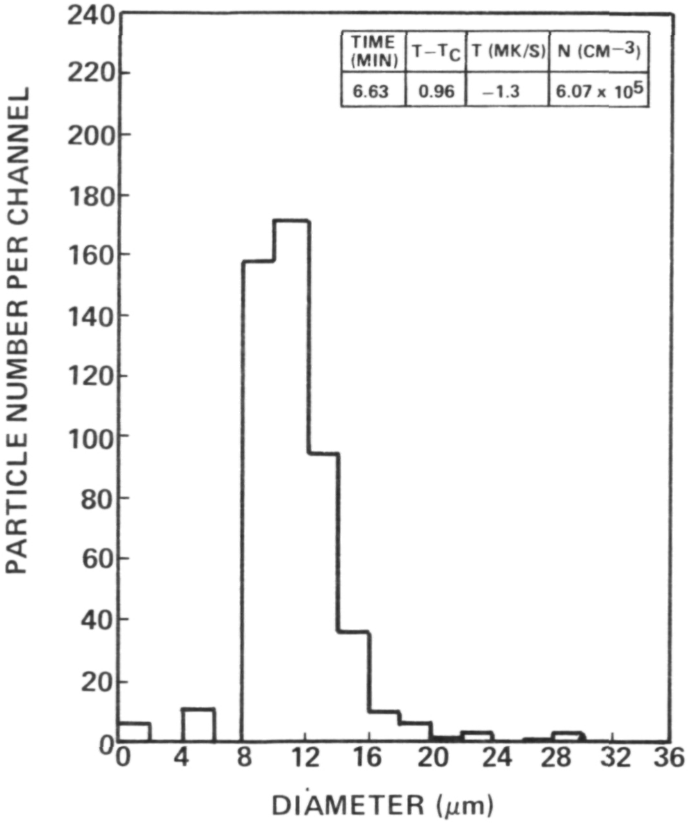
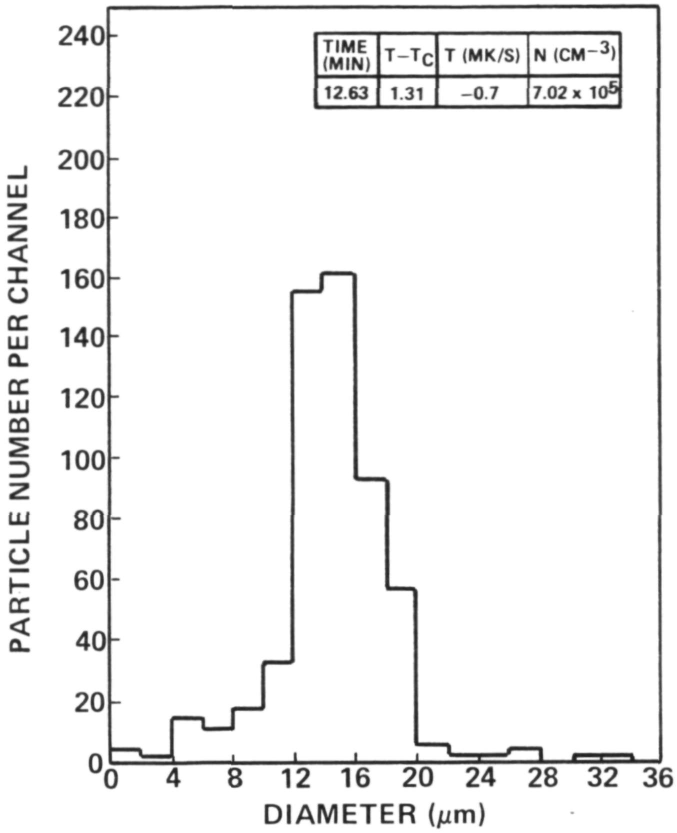
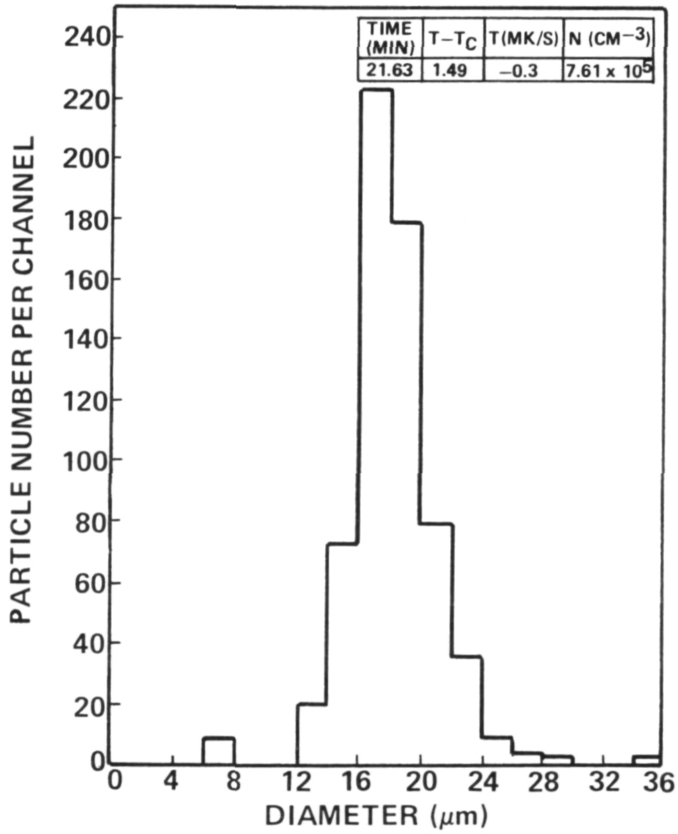


Figure 10b. Particle size distribution, hologram No. 115.



TIME (MIN)	$T-T_C$	T (MK/S)	N (CM^{-3})
12.63	1.31	−0.7	7.02×10^5

Figure 10c. Particle size distribution, hologram No. 116.



TIME (MIN)	$T-T_C$	T(MK/S)	N (CM^{-3})
21.63	1.49	−0.3	7.61×10^5

Figure 10d. Particle size distribution, hologram No. 117.

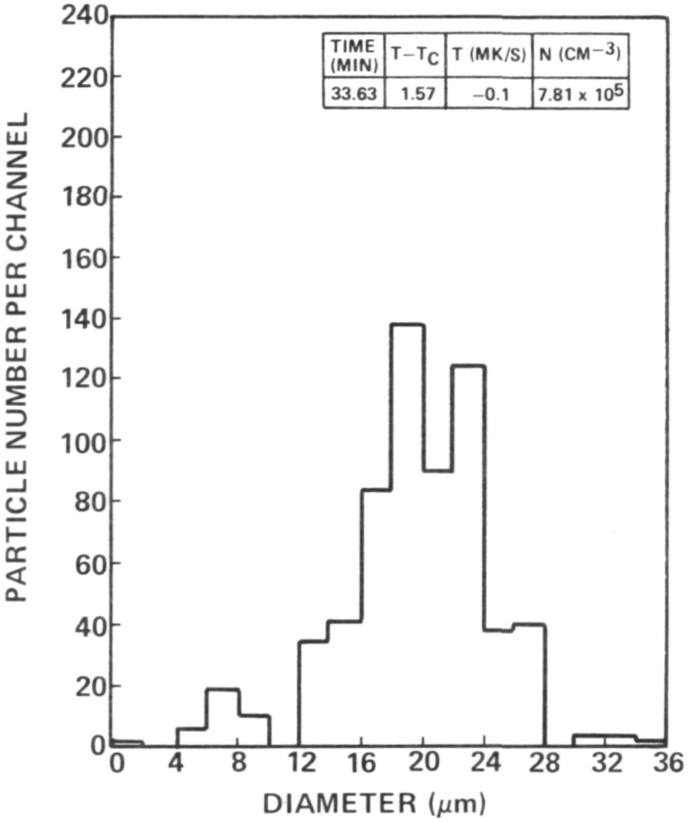


Figure 10e. Particle size distribution, hologram No. 118.

increases with time as the temperature of the test cell is gradually lowered. The growth rate initially goes as $t^{\frac{1}{2}}$ as would be expected in a diffusion process, but eventually falls off as the available second-phase material is depleted from the solution [21]. After several tens of minutes, the size distribution was observed to evolve into a more complex pattern with multiple peaks corresponding to fusion of two or more droplets. Thus, the holography provides us with a powerful method for studying agglomeration phenomena, as well as growth of the second-phase droplets.

The positions of selected droplets are determinable in three dimensions on successive holograms. This allows access to droplet velocities. In addition to the expected Stokes settling, the droplets observed were found to have a slight sideways drift. This is believed to be the result of a slow convective flow in the test cell, probably due to a very small temperature difference across the width of the cell.

In following the motion of these droplets, a curious phenomenon was observed. On several occasions, two or more droplets in close proximity appeared to be suddenly drawn together and coalesced into a single droplet. It is conjectured that overlapping diffusion fields around each droplet may result in solutal gradients that produce surface-tension-driven flows which drive the droplets together.

Subsequently, these studies will extend to succinonitrile-H_2O/D_2O which has a convenient monotectic temperature (18.8°C) and other systems of interest. Furthermore, observation of other growth and agglomeration phenomena may be possible. For example, agglomeration can be studied on a statistical basis from the size distributions, as well as on a mechanistic basis, by following actual particle trajectories. The extension of these studies to systems that can be solidified at convenient temperatures is necessary to obtain a complete data set for all aspects of monotectic solidification in a system that can be studied in detail.

An improved thermostatic control has been developed by Professor Goldburg (University of Pittsburgh) that is stable to 1 milli Kelvin. This will allow observation of nucleation and growth in an isothermal environment which should remove the previous complication of additional nuclei forming as the temperature varies. Also, since the succinonitrile system is adjustable to neutral density by varying the ratio of H_2O to D_2O, it should be possible to remove the agglomeration from Stokes settling and reproduce the situation encountered in low-g. Under these static conditions, effects such as Ostwald ripening, agglomeration due to overlapping diffusion fields, and possibly other effects can be isolated and studied. Variable cooling rates can determine how the nucleation density changes with temperature and extend the model to account for the more complicated, but realistic, situation encountered during the actual solidification process.

A computer model simulates the growth of the second-phase droplets [22]. Particles are randomly assigned coordinate positions and sizes commensurate with the observed number density and size distribution. Growth is obtained by solving the diffusion equation for a single particle in an infinite solute field [23]; however, the concentration of the solute field is allowed to decrease in time because of depletion due to the other particles [24]. A force law can be added to the particles to describe Stokes migration, thermal migration, or surface-tension gradients produced by overlapping particle fields. Agglomeration can be simulated by testing to see if coordinates of nearest-neighbor particles are such that the particle radii overlap. This model is in a development stage on a desk-top computer and has handled up to 500 particles and provided a reasonable simulation of the observed growth phenomena.

VI. SPINODAL DECOMPOSITION

The free-energy isotherms for a system with a liquid-phase miscibility gap must have double minima below the critical temperature. These minima correspond to boundaries of the two-phase region. Such isotherms also have two inflection points where the curvature changes sign. The locus of these inflection points on the phase diagram defines the spinodal [25]. If a system is cooled into the immiscible region outside of this spinodal, it can lower its free energy by decomposing into two liquid phases; but, since this requires a temporary increase in free energy, the system is metastable. Therefore, decomposition into the two liquid phases is by nucleation and growth by diffusion, as discussed in the previous section. Inside the spinodal, however, any density fluctuation lowers the free energy, and the system is completely unstable and will spontaneously decompose.

Since spinodal decomposition may dominate in systems with compositions that traverse the widest portion of the miscibility gap or in rapidly-cooled specimens, more information is required to define such a system at the onset of solidification. Application of the holographic techniques described in the previous section is useful to investigate spinodal decomposition. The spinodal can be reached without going through a metastable region by choosing the composition corresponding to the critical point. It may be possible to undercool compositions near the critical point into the spinodal without nucleation. It may also be possible to identify the spinodal, even if nucleation and growth have begun, if the cooling rate can be controlled well enough.

It is desirable to map out the location of the spinodal on the phase diagram and to observe the droplet number density, size distribution, and growth process associated with spinodal decomposition.

VII. SOLIDIFICATION STUDIES

Since the monotectic temperature of the DEG-ES system is much lower than ambient, it is not a convenient system for solidification studies. However, succinonitrile-H_2O is a very good system for this purpose. Succinonitrile ($C_4H_4N_2$) can be prepared in extremely pure form by zone refining and is well characterized in terms of physical properties [26]. Also, the $C_4H_4N_2/H_2O$ phase diagram is known (Fig. 11). This system has an additional advantage of having only a small density difference between the two phases. Furthermore, the two phases of the system can be equalized with respect to density at a specific temperature by substituting the appropriate amount of D_2O for H_2O. Unfortunately, density stabilization can only be accomplished at one temperature because of the differences in thermal expansion between H_2O and succinonitrile. Therefore, although density-driven separation may be minimized during a solidification process, it cannot be completely eliminated on the Earth.

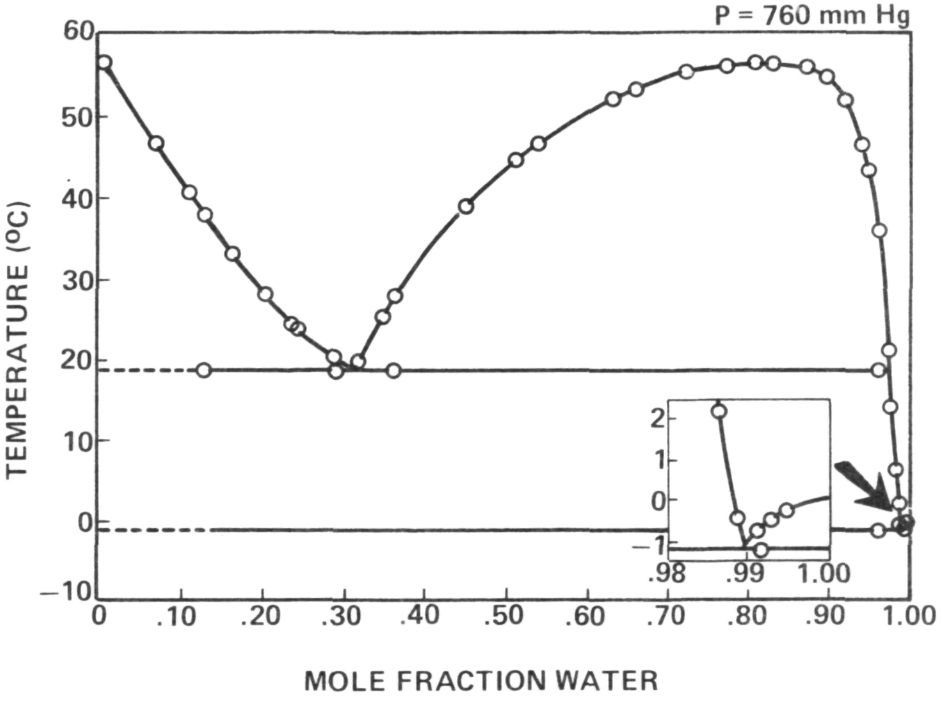
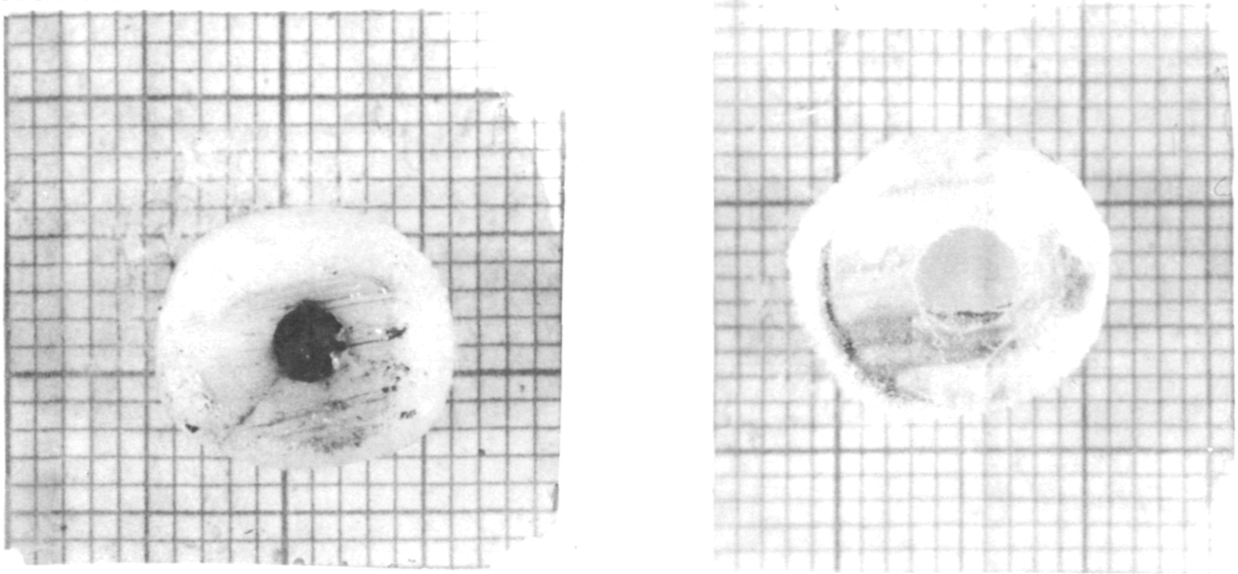


Figure 11. Succinonitrile-H_2O phase diagram.

Fast quenching studies of a concentration range of succinonitrile-H_2O/D_2O solutions in siliconized pyrex tubes (succinonitrile-rich phase preferentially wetting) and in plain pyrex tubes (H_2O-rich phase preferentially wetting) demonstrate the importance of viscosity to relative wetting and thermal migration effects [27]. In these studies, solution densities were adjusted to be neutral near the 18.8°C monotectic temperature.

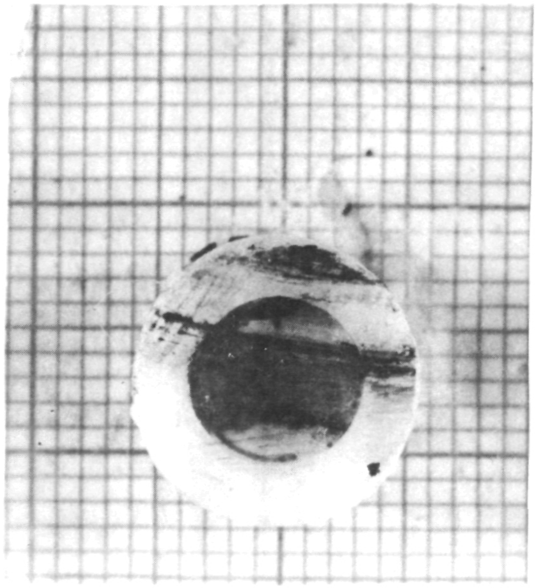
Heating the tubes above the consolute point homogenized the mixture and fast quenching proceeded by immersion of the tubes into liquid nitrogen.

Cross sectional slices (Fig. 12) reveal that massive separation did occur. The relative locations of the phases strongly depended on wetting properties and solution viscosities.



(a) Bottom of ingot
(annulus: 8.76 wt.% H_2O/D_2O)

(b) Middle of ingot
(annulus: 7.97 wt.% H_2O/D_2O)



(c) Top of ingot
(annulus: 7.99 wt.% H_2O/D_2O)

Figure 12. Cross-sectional slices of LN_2 quenched succinonitrile – H_2O/D_2O solution. Centers are lower melting H_2O/D_2O rich phase (monotectic composition: 9.4 wt.% H_2O).

Quenching studies with near neutral density systems offer a means of simulating low-g solidification, but it is difficult to observe precisely what is happening inside a quenched tube. Also, it is difficult to control or even predict the thermal environment during the process. The latter difficulty can be overcome by using directional solidification techniques.

Directional solidification offers the simplification of nearly unidirectional heat flow in the vicinity of the solidification front and provides an independent control of both growth rate and thermal gradient that is not available in ordinary casting techniques. A vertical Bridgman-Stockbarger "furnace" has been assembled (Fig. 13). The hot and cold zones consist of water jackets connected to thermostated baths. An adiabatic zone separates the two water jackets. This zone is purged with dry N_2 to prevent condensation and provides a controlled thermal gradient with reasonably flat isotherms as well as an observing station.

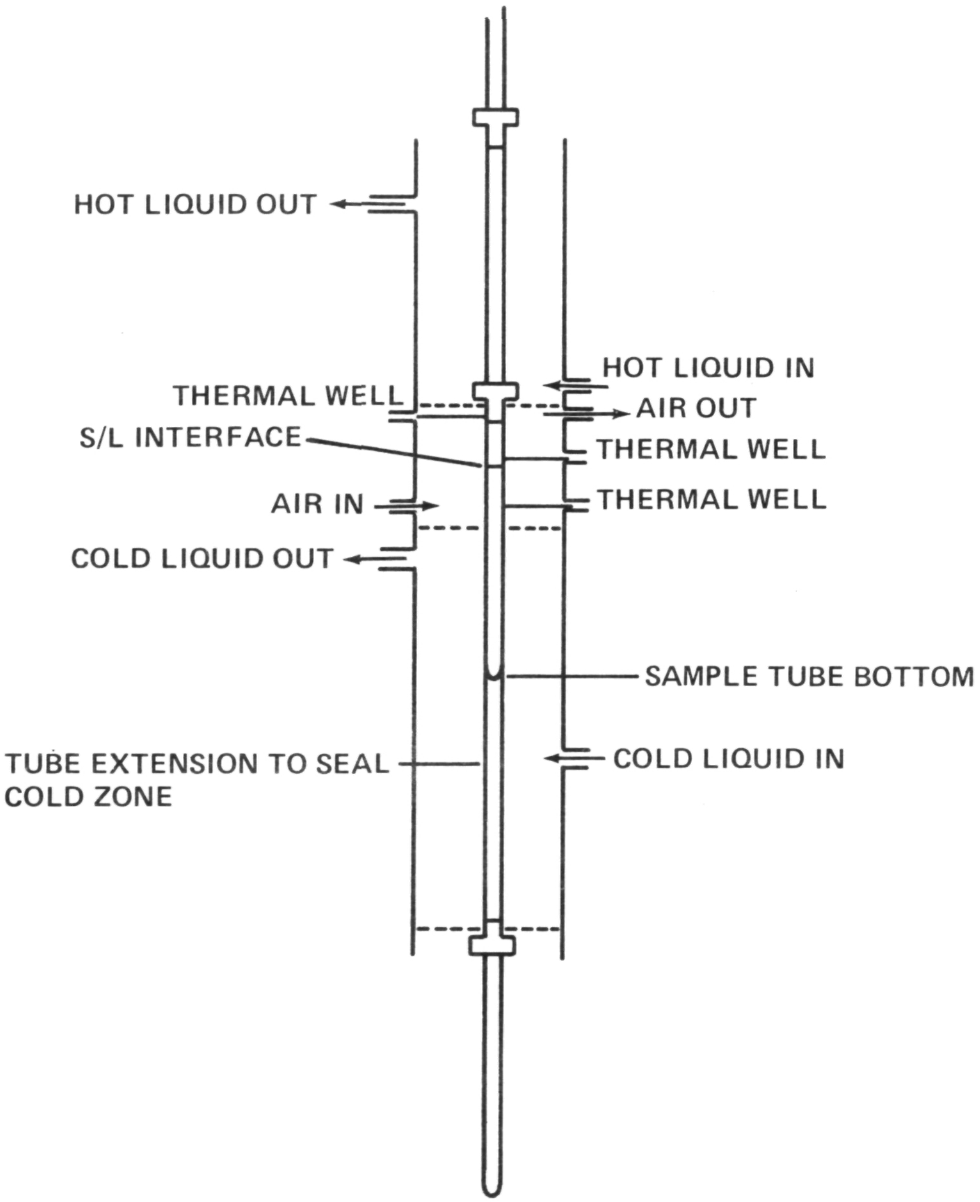


Figure 13. Bridgman-Stockbarger "furnace" for directional solidification of model solutions.

The Bridgman-Stockbarger furnace is useful to study the effects of gravity, solidification rate, and gradient in the phase separation process. By adjusting the amount of D_2O, the H_2O-rich phase can be made more dense or less dense than the succinonitrile-rich phase. Therefore, the effects of stable versus unstable solutal convection may be examined while maintaining a stable configuration against thermal convection. Also, since the thermal migration rate of second-phase droplets depends on thermal gradient, there may be a critical value of G/R (thermal gradient/growth rate) below which the interface advances faster than the migration velocity of the droplets. Since a large range of G/R ratios are possible in Bridgman-Stockbarger growth, such effects can be readily investigated.

Directional solidification experiments may also proceed in 1-cm-square spectroscopic cuvettes with thermoelectric heaters/coolers on each end. The system is initially heated above the consolute temperature and homogenized using both thermoelectric devices. Then the lower thermoelectric device is used to cool the bottom of the cuvette in a gradient-freeze mode. While this solidification technique does not provide as much control as the Bridgman-Stockbarger method, it has the advantage of accessibility to schlieren, interferometric, and holographic optical visualization techniques. Also, the cuvette and the optical system can be flown in ballistic aircraft to obtain data of the convective flows in high- versus low-gravity fields.

For detailed studies of the region around the solidification interface on a microscopic scale, a very thin (essentially two-dimensional) test cell may be translated across two temperature-controlled heating/cooling blocks and viewed with a microscope [28,29]. By adjusting the temperatures of the two blocks, a specific gradient can be achieved and the interface positioned within the field-of-view of the microscope. With this technique, the solid-liquid interface may be studied in detail. Hellawell observed the incorporation of the H_2O-rich liquid phase into the succinonitrile matrix for monotectic compositions with this technique [3]. Of particular interest in this study is the behavior of a hypermonotectic composition during solidification, especially the interactions between the excess minority phase and the solidification front. By orienting the thermal gradient stage vertically, the effect of density differences between the two phases may be investigated. The small width of the test cell effectively suppresses thermal convection arising from small, lateral-thermal variations, but fluids with different densities will ultimately configure themselves to minimize gravitational potential. Of particular interest is whether gravity modifies the concentration field just ahead of the solidification front. This question is also of interest to the solidification of eutectic systems and may shed some light on the recent unexpected result of Pirich and Larson [30] who found significantly different rod diameters and spacings in a directionally-solidified Mn-Bi eutectic in low-g as compared to samples solidified on Earth in the same furnace.

One unresolved question at this time is the problem of mapping the concentration fields on a microscopic scale. Conventional interferometry lacks sufficient sensitivity and resolution to detect the small changes in index of refraction in the thin sample required for observing the sample microscopically. Microscopic interferometry and phase-contrast microscopy are potential methods.

It is important to develop sufficient understanding of the phase separation process to allow predictions of the behaviors of metallic systems with the possibility of being able to control microstructures. Computer models developed on the basis of the transparent models will be applied to existing specimens prepared in low gravity currently in bonded storage at MSFC. Unfortunately, the bulk of the model systems studied to date are succinonitrile based which invalidates any attempt to immediately generalize observed phenomena to metallic monotectic alloys. Therefore, there is a need to expand the number of these transparent binary models to allow distinctions between unique and general phenomena. It is desirable to develop a rapid screening technique to find model systems of interest and then experimentally measure their phase diagrams. To simulate phase diagrams, two computer programs which determine solid-liquid and liquid-liquid equilibria are available. These programs use the UNIFAC (Universal Functional-Group Activity Coefficient) method to predict the activity coefficients and compositions associated with the solid-liquid and liquid-liquid portions of the phase diagrams on the basis of functional groups within the molecules [31].

It may be necessary to obtain additional data from the stored MSFC samples such as the macroscopic composition of the separated phases. Application of model results to explain distribution of phases in metal alloys should be applicable to post-flight analysis of samples to solidify during Shuttle flights by Gelles and Potard. Additionally, various metallic samples will be prepared and solidified in the MSFC drop tower to test various predictions from the models.

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APPROVAL

SEPARATION PROCESSES DURING BINARY MONOTECTIC ALLOY PRODUCTION

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William K. Witherow, and Ursula Fanning

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

AJ Dessler

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