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Solidification under microgravity

B K DHINDAW

Metallurgical and Materials Engineering Department, Indian Institute of Technology, Kharagpur 721 302, India
e-mail: dhindaw@metal.iitkgp.ernet.in

Abstract. The paper outlines the broad areas where studies are being conducted under microgravity conditions worldwide viz., biotechnology, combustion science, materials science and fluid physics. The paper presents in particular a review on the various areas of research being pursued in materials science. These include studies on immiscibles, eutectics, morphology development during solidification or pattern formation, nucleation phenomena, isothermal dendrite growth, macrosegregation and the behaviour of insoluble particles ahead of the solidifying interface. The latter studies are given in detail with description of case studies of experiments conducted by the author on space shuttles. In particular, the technology and the science issues are addressed. Lastly, based on the presentations, some salient features enumerating the advantages of conducting experiments under conditions of microgravity are highlighted in terms of science returns.

Keywords. Microgravity; solidification; space shuttle; experiments.

1. Introduction

Currently focus has shifted to the use of a microgravity environment, where buoyancy driven convection and sedimentation need to be eliminated to validate physical models, as compared to space manufacturing. One of the areas that has emerged as the forerunner in such studies is solidification science. This is an obvious choice since solidification processing is an important step in most of the fabrication techniques where the starting stock has to be cast as ingots. Apart from this, most of the theories developed to describe the solidification phenomena are based on the assumption that solidification takes place under no-convection conditions (Kurz & Fisher 1986) though this is implicit and not directly stated. This is mostly because analytical models are difficult to develop if convection is introduced.

Before detailed discussion is initiated on the solidification phenomena, it would be of interest to enumerate the other broad areas where studies are being conducted under microgravity.

Biotechnology: Crystal growth of biological macro-molecules, and cell and molecular science, focusing in particular on proteins and viruses, is fast emerging as an important area of research in microgravity.

Combustion science: Combustion science research programme focuses on understanding the important processes of ignition, propagation and extinction during combustion in low gravity.

Materials science and fluid physics: The purpose of the microgravity fluid research programme is to improve our understanding of how the presence of gravity either limits or effects the fundamental behaviour of fluids, in terms of both dynamics and transport. It also helps in the study of gravity-dependent fluid phenomena in other microgravity science disciplines such as materials science and combustion. In materials science research, the unique characteristics of space influence material solidification and crystal growth. This paper discusses in detail the solidification of materials in the microgravity environment of space.

As stated earlier, the phenomenon that is expected to be most influenced in microgravity is phase transformation from liquid to solid occurring during the process of solidification.

A brief review of the following research programmes conducted in microgravity would indicate its relevance in any materials science research programme, especially solidification studies.

- Effect of convection on morphological stability during coupled growth in immiscible systems.
- Processing of eutectics in microgravity.
- Melt interface stability during solidification studied by Seebeck coefficient variation in MEMPHISTO facility.
- Interface undercooling, solidification velocity and nucleation.
- Isothermal dendritic growth experiment to study undercooling effect on growth kinetics.
- Pushing/engulfment transition in insoluble particles dispersed material systems.
- Macro-segregation in alloys.

2. Coupled growth in immiscible alloys

The overall objective of the coupled growth of monotectics is to study the physics of the solidification in immiscible alloy systems. The monotectic reaction ($L_1 = a + L_2$) which occurs in many immiscible systems should make it possible to produce aligned fibrous composite structures through directional solidification. However, to investigate the mechanism of aligned structure formation, a convection-free environment is required, as recent studies have indicated that the gravity level has dramatic influence on the structures obtained during directional solidification (Andrews *et al* 1991). Testing of existing models require directional solidification of a range of alloy compositions at several solidification rates. Due to the tendency towards sedimentation in these immiscible systems and the possibility of convective instability, experimentation was perceived to be better if carried out under low-gravity conditions. Flows generated by convection and the resulting composition variations in the sample strongly affect the ability to maintain a macroscopically planar solidification front. Experiments were carried out on the space shuttle during the Life and Microgravity Spacelab (LMS) mission on Al–In alloys in AlN crucibles. One of the significant features of the experiment was the specially designed ampoule for encasing the samples. The experiments demonstrated (Andrews & Coriell 1998) that solidification of monotectics under microgravity is complicated due to the wetting behaviour and its strong influence on the solidification.

3. Processing of eutectics in a microgravity environment

Experiments conducted so far under microgravity suggest that convection influences the solidification of an important class of materials termed eutectics. Future programmes (Larson 1996) would include efforts to investigate the Jackson–Hunt theory with respect to kinetic effects at the solidification interface. The theory has been advanced that the interface composition may be unequal to the bulk eutectic composition in some cases. This, in turn, can lead to interaction with the macroscopic fluid flow field. This theory includes interface under cooling, which is velocity dependent. The ‘advanced’ theory predicts convective influence, resulting in compositional and structural refinement. The advanced theory is being experimentally validated in the interest of developing a ‘universal’ theory that can explain all the microgravity results and which can be used to predict results of future experiments under one-*g* and low-*g*. Advanced techniques like Peltier pulsing and Seebeck interfacial temperature characterisation would be used to study parameters. The Seebeck effect application in determining interface stability is discussed in a later section.

4. *In situ* monitoring of crystal growth by seebeck coefficient measurement

For an alloy ΔT_c, constitutional undercooling, primarily contributes to the total undercooling. The contribution of kinetic undercooling is only significant in faceted materials and that of curvature for morphologies with radius less than 10 μm. ΔT_c is of paramount importance in several solidification phenomena.

4.1 *Theory*

According to the constitutional supercooling criterion, the critical growth velocity V_c above which the planar interface is no longer stable and transforms to a cellular morphology is related to the interfacial undercooling according to the relationship,

$$G_l/V_c \geq \Delta T_c/D_l,$$

where, G_l = temperature gradient ahead of the S/L interface, D_l = diffusion coefficient,

$$\Delta T_c = mC_o(1-k)/k,$$

where, k = partition coefficient, m = slope of the liquidus.

For verification of any theory related to morphological stability, it is important to experimentally quantify, undercooling at the interface. Apart from plane front solidification, experimental measurement of interfacial undercooling is also necessary to characterise the morphology of a cellular growth front. Burden & Hunt (1974) related the cell tip undercooling to thermophysical parameters and solidification variable as,

$$\Delta T_c = \frac{G_l D_l}{V} + A\left[\frac{mVC_o}{D_l}(k-1)T_m q\right]^{0\cdot 5},$$

where T_m = is the equilibrium melting temperature, $A = 5\cdot 6$ or $2\cdot 8$ depending on whether marginal stability or minimum undercooling criterion is used,

$$q = g/L,$$

where, L = latent heat, g = interfacial energy.

4.2 *Experiment*

Conventional probes such as thermocouples due to their large bead size often do not have sufficient resolution for measuring undercooling at the S/L interface to adequately test theory. Further the intrusive nature of the thermocouple can distort the thermal field at the S/L interface. To overcome these inherent problems a non-intrusive technique utilizing the difference in Seebeck coefficient between the solid and the melt was used to precisely measure ΔT at the S/L interface. The technique (Sen *et al* 1998) essentially consists of melting the central portion of a sample and thereby generating two S/L interfaces, one at either end. One of the interfaces is kept stationary while the other is translated at a fixed velocity. The Seebeck emf, E_s, generated between these two interfaces can be directly correlated to the interfacial undercooling by the expression,

$$E_s = h_{sl}\Delta T,$$

where, h_{sl} is the Seebeck coefficient between the solid and the liquid.

Temperature depression due to compositional change at the interface for a purely diffusive state can be calculated using the classical approach. The governing equation for the plane front solidification in initial transient under steady state conditions is given as,

$$C_l^* = C_o\left\{\frac{1-k}{k}\left[1-\exp\left(-k\frac{V}{D_l}x\right)\right]+1\right\},$$

where C_l^* = solute concentration at distance x, C_o = bulk solute concentration.

The chemical contribution is then given by,

$$\Delta T = m_l(C_l^* - C_o),$$

where C_l is the composition of the liquid at the interface, C_o is the initial alloy composition, k is the equilibrium partition coefficient, V is the growth velocity, D_l is the liquid diffusivity, x is the distance solidified and m_l is the liquidus slope. If the overall undercooling is known and solutal undercooling under purely diffusive conditions, possible only in convection-free microgravity environments, is also known, then kinetic undercooling especially for a faceted interface can be determined by detecting kinetic undercooling due to dislocation assisted growth given as

$$V = a\,\Delta T_k^{\,n}.$$

Measurement of Seebeck coefficient at the melt interface under microgravity conditions, where convection is absent, is used to truly characterise the stability criteria validation. Several experiments have been carried out in the MEMPHISTO facility aboard the space shuttle to carry out such studies successfully.

4.3 *Pattern formation during solidification*

Connected with the above is the important study on the pattern formation (Billia & Trivedi 1993) in microstructure development during solidification. During the directional solidification of a binary alloy, three experimental parameters control the morphology of the solid–liquid interface and the growth rate. If the first two factors are held constant, at slow growth velocities, the solidification front is planar. As the rate increases above a critical value, the interface forms a cellular microstructure which becomes dendritic at higher growth velocities. This pattern formation is associated to the Mullins–Sekerka instability and much effort has been devoted to predict the characteristics of the cell or dendritic arrays as a function of the solidification control parameters. Attempts are often made during directional solidification studies to eliminate buoyancy convective motion in the liquid phase that can mask some important physical mechanisms. Even in a vertical configuration where these effects are minimal, radial effects can cause convective motion disturbing cellular growth regimes. Thus verification of the various models describing the pattern formation is not possible conclusively under terrestrial conditions. Thus experiments have been initiated under microgravity conditions aboard the space shuttle on binary Al–Ni alloys. Essentially solute concentration profiles in various regimes of solidification have been measured and compared with those obtained at ground conditions.

5. Nucleation theory and microgravity requirements

The factors that influence the nucleation behaviour of a material are important to understand for both scientific and practical reasons (Bayuzick & Rabinson 1996). In practical terms, the study of nucleation and the accompanying impacts of undercoolability and rapid solidification in obtaining unique phases and/or microstructures have the potential to help in making significant advances in material processing. From the work of Fisher and Turnbull and the assumption of a spherical embryo the following equation has been developed describing nucleation,

$$J_v \approx 10^{33} \exp[-16 p s_{ls}^{3} / (3 \Delta G_n^2 kT)],$$

where J_n = volume nucleation rate, 10^{33} = exponential factor, T = temperature, k = Boltzman’s constant, ΔG = activation energy for nucleation, s_{ls} = interfacial free energy between parent and daughter phase.

In most nucleation experiments, heterogeneous nucleation is assured by either intrinsic or extrinsic impurities. Heterogeneous sites reduce the solid–liquid interfacial free energy barrier by some amount proportional to the wettability of the impurity. The pre-exponential also decreases in heterogeneous nucleation by a factor proportional to the available heterogeneous site. Also since classical nucleation theory is a theory of thermodynamic fluctuations, particular attention is placed on the effect of flow in the melt on undercooling. Owing to the two factors above, experiments done on the earth using levitation techniques and also so far under microgravity have given experimental results with which it is difficult to validate theoretical propositions. Ground experiments raise the possibility of complex flows, while contamination effects from the surroundings have hindered the microgravity experiments.

5.1 *Nucleation and solidification characteristics*

Similar to the above studies in directional solidification of inoculated alloys under diffusive transport conditions, transition from columnar to equiaxed grain structure is predicted to occur continuously through intermediate mixed structure as a function of the density of the nuclei N_o, temperature gradient G and solidification rate R (Hunt 1984). Hunt's model could not be verified experimentally because, in practice, gravity-driven convection affects these three parameters. For this reason more recent models try to include convective effects. However, in order to assess the models, experiments able to separate convection from the other mechanisms are still needed. This has led to conducting experiments in microgravity environment on inoculated Al–Cu alloys to minimise convection so that diffusive transport mechanism is dominant and in which density of the nuclei N_o is controlled through refiner content. From these experimental results Hunt's model can be checked as well as the mechanism of cellular to equiaxed transition.

5.2 *Theory*

Briefly, a transition from a mixed to a fully equiaxed microstructure is predicted according to Hunt's (1984) model, when

$$G_l < 0{\cdot}617 N_o^{1/3}[1 - (\Delta T_N/\Delta T_c)^3]\Delta T_c,$$

where, G_l = temperature gradient in liquid, N_o = number of nucleating sites per unit volume, ΔT_n = nucleation undercooling, ΔT_c = columnar undercooling.

If ΔT_n can be neglected compared to ΔT_c, the above relation simplifies as follows,

$$G < 0{\cdot}617 N_o^{1/3}(VC_o/A)^{1/2},$$

given,

$$\Delta T_c = (RC_o/A)^{1/2}.$$

5.3 *Experiment*

The microgravity experiments have shown (Dupouy *et al* 1998) a continuous transition from a purely equiaxed to an anisotropic solidification microstructure as a function of solidification rate and the local temperature gradient at the front. Conditions for the transition have been found to somehow depart from the ones predicted by the simple model. In addition, the aspect of the anistropic microstructure was not the same as anticipated in the model. One of the other causes that changes the microstructure in the ground solidified samples is the settling of the nucleants that does not occur in the microgravity environment. Also the equiaxed crystals can move due to convection in ground experiments.

6. Effect of undercooling on kinetics of dendrite growth

Growth of dendrites is one of the commonly observed forms of solidification encountered when metals and alloys freeze under low thermal gradients, as occurs in most casting and welding processes. In engineering alloys, details of dendritic morphology directly relate to important material responses and properties. Of more generic interest, dendritic growth is also an archetypical problem in morphogenesis, where a complex pattern evolves from simple starting conditions. Thus, physical understanding and mathematical description of how dendritic patterns emerge during the growth process are of interest to both scientists and engineers.

6.1 *Theory*

A number of theories of dendritic crystal growth, based on various transport mechanisms, physical assumptions, and mathematical approximations have been developed over the last fifty years. These theories attempt to predict tip velocity, V, and radius of curvature, R, as functions of the supercooling, ΔT. Growth of dendrites in pure metals is known to be controlled by transport of latent heat from the moving crystal-melt interface as it advances into its supercooled melt. Experiments with SCN show that gravity-induced convection dominates dendritic growth in the lower supercooling range typical of metal alloy castings (Glicksman & Huang 1982). Convection unfortunately confounds any straightforward analysis of dendritic solidification based on conductive heat transfer. There have been a few attempts to estimate the effect of natural or forced convection on dendritic growth, but these calculations are themselves based on yet unproven elements of dendritic growth theory, and, consequently, cannot provide an independent test of the theory. In the higher supercooling range, where thermal convection influences diminish in comparison to thermal conduction, the morphological scale of dendrites becomes too small to be resolved optically at the reported growth speeds encountered. The experimental situation prior to the microgravity experiment was that there appeared to be too narrow a range of supercooling in any crystal-melt system studied terrestrially that remains both free of convection effects, and also permits accurate determination of the dendritic tip radius of curvature.

6.2 *Isothermal dendrite growth experiments*

The Isothermal Dendritic Growth Experiment (IDGE), a NASA sponsored series of Space Shuttle microgravity experiments, was designed to grow and photograph dendrites in the absence of convective heat transfer for fundamental tests of dendritic growth theories. Data and subsequent analyses on dendritic tip growth speeds and sizes from the IDGE have demonstrated that although the theory can make predictions that are in reasonable agreement with the results of the experiments, there are several important areas of disagreement. In the lower supercooling range where convection does not influence the growth parameters, the theories are well-supported by the theories, however, in the higher supercooling range theories need to be modified. Apart from this, the occurrence of the side branching mechanism of dendrites needs to be accurately investigated with further study of thermodynamic parameters like the entropy of fusion.

7. Pushing engulfment transition in insoluble particle dispersed solidifying systems

Experimental evidence demonstrates that there exists a *critical velocity* of the planar solid/liquid (SL) interface below which particles are *pushed* ahead of the advancing interface, and above which particle *engulfment* occurs. Applications for this kind of fundamental research can be found in the area of superconductors, biological cell preservation, and geology. However, the major portion of the research work involving particle pushing is aimed at metal matrix composites (Stefnescu *et al* 1988). Only with homogeneous distribution of the reinforcing phase can the improved mechanical properties of these materials be fully exploited. Over the years, numerous models have been proposed in attempts to explain particle behaviour at the S/L interface. Most of the models solve the balance between the drag force exercised by the liquid on the particle (which pushes the particle into the interface), and the repulsive force between the particle and the S/L interface (the interface interaction force). The influence of melt convection on the particle-interface interaction is ignored.

7.1 *Theory*

There are several theoretical models describing this phenomenon. The significant amount of theoretical and experimental work suggests that there exists a relationship of the type given below, in one of the models, between critical velocity and particle radius (Stefanescu *et al* 1997)

$$V_{\mathrm{cr}} = (\Delta g_o a^2_o/(3hK^*R)),$$

where

Δg_o = surface energy difference between particle/solid and particle/liquid, h = liquid viscosity, $K^* = K_p/K_{\mathrm{l}}$, is the ratio between the thermal conductivity of the particle (K_p) and of the liquid(K_l), a_o = atomic diameter.

Although the theoretical effect of convection on the critical velocity has been shown, it is based on parameters difficult to estimate. If a particle is situated in front of a solid/liquid interface and the fluid has convective movement, Saffman force is exerted on the particle. Depending on the direction of the flow of the fluid the particle may experience a lift force or a force pushing the particle into the interface. The Saffman force is defined by the equation given below:

$$F_s = 6{\cdot}46 m V_{rel} R^2 (S_{\mathrm{avg}}/n)^{1/2},$$

V_r = velocity of movement of particle, S_{avg} = average velocity gradient, v = kinematic viscosity.

This force is based on difficult-to-calculate parameters, like velocity gradients in the fluid. Therefore to experimentally evaluate the critical velocity of engulfment, experiments need to be conducted in convection-free environment.

7.2 *Experimental*

The system chosen for experiments had to satisfy several requirements, both from the point of validation of the models and also from the requirements of conducting experiments in the microgravity environment obtained abroad the space shuttle. For example, for validation of the model the particles should be spherical. For the requirements of model and microgravity conditions there should be no influence of marangoni convection on the measurement of critical velocity. Both the latter requirements are taken care of by suitable design of the ampoules for encasing the samples. Figure 1 gives the design of the ampoule used in the LMS mission STS-78 in June 1996.

In the experiments conducted on the STS-78 mission (Juretzko *et al* 1997), differences in the critical velocities as measured on ground and in space was indeed observed. As far as possible, experiments on the ground and in space were conducted under identical conditions, except for the gravity effects.

Similar experiments have been conducted on transparent matrix systems under microgravity conditions. The systems investigated included succinonitrile dispersed with polystyrene particles and biphenyl dispersed with glass particles. The experiments were conducted during the space shuttle mission STS-97 in November 1997. The main purpose of the experiments was to establish a relationship between critical velocity and the particle radius and verify the model of particle pushing. The experiments established the differences in experimental critical velocities on ground and in convection-free microgravity environment. However, data could not be obtained for critical velocities for particles below 2 μm diameter.

In these experiments an interesting phenomena was observed that may throw new light on interparticle forces. The particles tended to agglomerate into large conglomerates in the liquid melt. Figure 2 shows (Sen *et al* 1999) the agglomerates as seen on the video downlink during the experiments. In the absence of convection in the space experiments the interparticle forces originating from interfacial forces may become significant causing agglomeration. This was more predominant in non-wetting systems like succinonitrile–polystyrene.

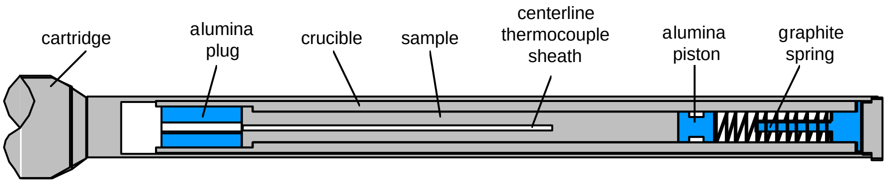

Figure 1. Spring loaded piston compensates for solidification shrinkage in cartridge ampoule design.

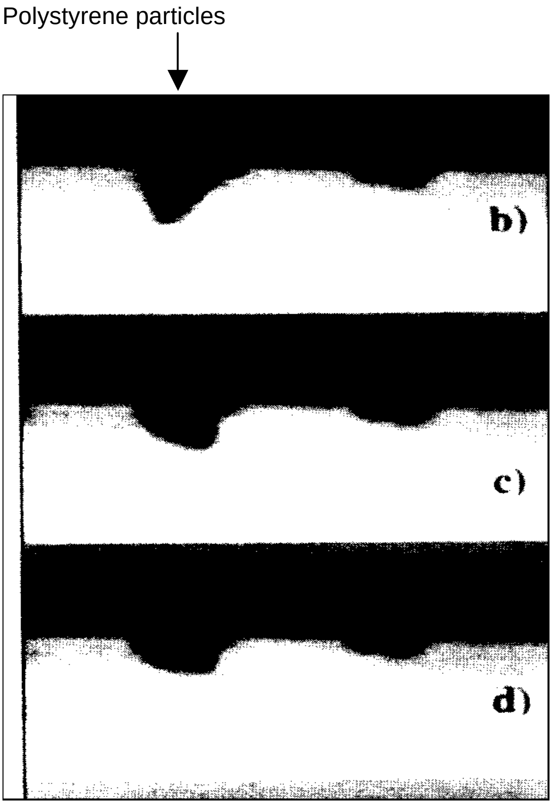

Figure 2. Polystyrene particles agglomerates in front of solidifying succinonitrile melt in microgravity environment.

8. Macrosegregation

Another major area in solidification research where convection plays an important role is macro segregation. The redistribution of solute in the matrix during solidification is of significant relevance owing to its leading to a wide range of casting defects. Macro segregation is one such phenomenon, which leads to poor quality castings. There exist numerous numerical and analytical models describing the macrosegregation phenomena. However reliable experimental data to validate these models are lacking. What the experiments so far have brought out is that convection strongly affects macrosegregation, but fails to quantitatively provide data that can truly represent the assumptions and conditions under which the models are developed. Therefore, there is a need to simplify the models by removing the convective effects that in any case can be included only in numerical models, and then to verify the model by carrying out experiments under convection-free environment in microgravity.

8.1 *Experimental*

Recently some experimental data from space shuttle experiments have been shown (Yu *et al* 1997), where in some parts of the solidified Al–38wt%Cu sample, macrosegregation is shown to be absent. However, the data are too few to draw any conclusive evidence or to verify any model. The authors have done some experiments in an isothermal casting furnace mounted inside DC-9 aircraft. Since low gravity is achieved in these aircraft during maneuvers only for periods of 20 s, it was again difficult to isolate the exact effect of low gravity on the macro segregation patterns although good qualitative results were obtained.

9. Summary and conclusions

Solidification-related transformations are significantly affected by the gravity level. The paper has discussed the effect of gravity on seven important areas of solidification science. It was shown that as the experiments have been initiated in solidification science in micro gravity, new and interesting results have led to opening of new directions and areas of research. Experiments are being conducted for the past three decades and new ones have been initiated during the past few years. Definitive differences have been seen in the results of experiments conducted in microgravity and on ground, when all other conditions are the same. However proper design of experimental set-up and details is mandatory for the success of the microgravity experiments.

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