Phase Selection in the Mushy-zone: 

LODESTARS and ELFSTONE Projects

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Abstract. In a collaboration sponsored by ESA and NASA, international partners have developed a work plan to successfully address key issues relating to understanding the role of convection on alloy phase selection for commercially important structural alloys using the MSL-EML facility aboard the International Space Station. The approach is two-pronged. First, ground and space-based experiments will develop a baseline database to anchor subsequent modelling predictions. Tasks include sample preparation and verification, ground-based transformation evaluation, space-based experiments, and thermophysical property evaluation to support modelling activities. Second, modelling and theoretical analysis tasks will lead to a new understanding of the role of convection in phase selection for this class of materials. These models will allow prediction and control of microstructural evolution during solidification processing. Tasks include modelling of macroconvection induced by the EM levitation field, modelling of microconvection within the dendrite array, nucleation modelling, and modelling of the transformation kinetics specific to each alloy system. This paper outlines how two NASA-sponsored projects relate to the goals of the international collaboration.

1. Introduction

Recent advances in computerized simulation of metal casting processes allows investigators to visualize fluid flow, melt convection, channeling, and transient heat flux distribution to provide accurate predictions for process control, evolution of microstructures on a local level, and product quality. Of particular importance is the fidelity of measurements of the thermophysical properties of the melt. Evaluation of key properties near the melting temperature is challenging due to the high fluidity and reactivity of molten metal alloys. Use of containerless levitation processing techniques allows for precise measurements while minimizing the potential for melt contamination for samples in both superheated and undercooled condition [1].

Confidence in model predictions requires a better understanding of material properties. Progress in process control requires advancement in both. Feedback between experiments and simulation drives technology improvement with an emphasis on understanding the development of defect structures and evolution of localized microstructural domains. Thus, two essential components must simultaneously be addressed:

- Improve the quality of thermophysical property measurements to anchor model prediction with controlled experimental verification.
- Develop physical models to describe how fundamental processes such as phase selection and evolution of solidification structures influence local product properties.
This paper outlines efforts by the international community to organize programmatic structures to support the establishment of collaborative investigation of these two components and illustrates how this approach has been put into practice by two teams of investigators. This effort involves a broad range of activity including theoretical evaluation, multi-scale modeling, and experimental verification.

2. International collaborations
The European Space Agency (ESA) solicited proposals in September 2009 to encourage formation of International Topical Teams to address critical scientific needs to be addressed using facilities onboard the International Space Station (ISS). The goal was to reach out to the broader scientific community to consolidate research activities and foster collaborative global teamwork. AO 2009 PHYS-BIOSR identified several key topics including questions specific to materials science investigations. Two questions are highlighted in that they relate to use of the multiuser Material Science Laboratory Electromagnetic Levitation (MSL-EML) facility located in the Columbus module

- What are the thermophysical properties of high temperature melts?
- What is the influence of convection on the formation of different microstructures in alloys?

This framework resulted in the establishment of a number of topical teams requiring space-based containerless levitation processing experiments to facilitate achieving their specific scientific goals.

The International Topical Team on Thermophysical Properties (Thermolab ISS) was established under the leadership of Hans Fecht to specifically address the first of these two questions. Team members concentrate on ground and space-based investigations to develop a baseline database to anchor model predictions. Tasks include sample preparation and verification, ground-based transformation evaluation, space-based experiments, and thermophysical property evaluation to support modelling activities.

The International Topical Team on Solidification (SOL-EML) was established under the leadership of Dieter Herlach to address the second of these two questions. Team members concentrate on modelling and theoretical analysis tasks which lead to a new understanding of the role of convection in phase selection. These models will allow prediction and control of microstructural evolution during solidification processing. Tasks include modelling of macroconvection induced by the EM levitation field, modelling of microconvection within the dendrite array, nucleation modelling, and modelling of the transformation kinetics specific to a broad range of alloy systems.

The synergy attained through marriage of these two efforts satisfies the two essential components required for accurate process control modelling. Two NASA projects support these activities. The LODESTARS project (Levitation Observation of Dendrite Evolution in Steel Ternary Alloy Rapid Solidification) looks at phase selection in commercially important structural steel casting alloys with an emphasis on developing a thermophysical property database to improve and control microstructural evolution; the project involves collaboration with the Thermolab-ISS topical team. The ELFSTONE project (Electromagnetic Levitation Flight Support for Transient Observation of Nucleation Events) was established as part of the ESA PARSEC project (Peritectic Alloy Rapid Solidification with Electromagnetic Convection) [2] under the leadership of Thomas Volkmann and Douglas Matson to look at the role of convection in phase selection; these projects involve collaboration with the SOL-EML topical team.

3. Mushy-zone transformations
The mushy-zone is a two-phase region where solid and liquid exist in pseudo-equilibrium. When a molten metal is undercooled, the fraction solid that forms can be predicted by the Stefan Equation

\[ C_p \Delta T = f_s \Delta H \]  

(1)
where \( C_p \) is the specific heat, \( \Delta T \) the undercooling, \( f_s \) the fraction solid and \( \Delta H \) the latent heat of fusion. For short periods of time, limited heat is rejected to the environment and the fraction solid remains constant, although other processes can occur within the mushy-zone which profoundly influences the final microstructure. For some alloy classes, a metastable solid may form prior to conversion to the stable solid phase; often arising from surface energy considerations. The metastable mushy-zone solid then acts as a heterogeneous nucleation site for the stable phase [3]. Competitive nucleation and growth determine the phase composition of the final material [4].

Two classes of liquid/solid phase transformation show remarkably similar behaviour. Ternary FeCrNi steel casting alloys are eutectic systems where a cooling liquid forms two solids from the melt. During undercooling of hypoeutectic alloys two types of mushy-zone can form – the metastable body-centered cubic (bcc) ferrite or the stable face-centered cubic (fcc) austenite. [5-7] As seen in the metastable phase diagram shown in Figure 1, these alloys show significant solute partitioning and solute rejection is extremely important during solidification. When the metastable phase forms the mushy-zone, nickel is rejected while chromium is enriched and the liquid is solute lean. When the stable phase forms later, the opposite happens. Thus, clusters forming in the mushy zone do so in an environment which is solute lean.

Soft magnetic FeCo alloys are peritectic systems where a cooling liquid forms a solid and a liquid from the melt. The solid forms may be either metastable bcc or stable fcc as was the case for the steel alloys but the influence of solute partitioning is opposite that observed previously. As seen in Figure 2, as the mushy-zone forms solute is rejected to the liquid and the growing clusters do so in an environment that is solute rich. This behaviour is seen not only in FeCo alloys [8] but also in FeNi [9], which show limited partitioning, and TiAlNb(Ta) peritectic alloys[10], which show significant partitioning.

Figures 1 and 2 show that in order to access the metastable phase there must be some critical undercooling achieved. During formation of the mushy-zone the temperature of the undercooled liquid rises to the intermediate plateau temperature. After a brief delay, the stable phase nucleates within the mushy-zone and the temperature rises again. This process is known as double recalescence [11] and all residual metastable phase is consumed through engulfment, melting, and resolidification into the stable phase.
Both the critical undercooling and the transformation delay are influenced by melt convection \cite{2}. Understanding how convection influences nucleation within the mushy-zone is the unifying theme for the LODESTARS and ELFSTONE projects.

4. Nucleation kinetics

The delay between recalescence events is commonly known as the incubation time and this represents how long it takes to develop nuclei of the stable phase. Convection significantly influences the incubation time during which the fcc phase clusters form on the bcc scaffold and grow to critical size to thus become stable. In classical nucleation theory \cite{12-14}, the steady-state nucleation rate, $I_s$, and time dependent nucleation rate, $I$, are related by the equations

\[ I = I_s \exp \left( -\frac{\tau}{t} \right) \text{ for } I_s = I_0 \exp \left( -\frac{\Delta G^*}{k_B T} \right) \]

where $\tau$ is a characteristic incubation time, $t$ the observed delay time, $I_0$ a pre-exponential factor, $\Delta G^*$ the Gibbs free energy for formation of a critical nucleus of $n^*$ atoms of a pure material, and $T$ the transformation temperature. The Boltzmann constant has a value of $k_B = 1.38 \times 10^{-23}$ J/atomK. Steady-state nucleation does not become appreciable until $\Delta G^* > 60 k_B T$ while transient nucleation does not become appreciable until $t \gg \tau$. Turnbull estimated that for condensed phases the incubation time was a function of the size of the cluster and the rate at which atoms cross the interface, $\beta^*$, between the surrounding matrix and the cluster \cite{15}.

The attachment rate $\beta^*$ has variously been related to the jump frequency \cite{15} and the lattice diffusivity \cite{14, 16, 17}. By invoking the principle of time reversal, where the statistical fluctuations in cluster size follow the same path during growth and decomposition, Feder et al. \cite{18} determined the incubation time to be

\[ \tau = \frac{(n^*)^2}{\beta^*} \]

Russell \cite{19} evaluated condensed phase nucleation for binary systems to account for the influence of solute partitioning and found that clusters approaching the critical size were surrounded by an enriched solute shell, contrary to expectation, and that diffusivity of the slower moving species controls the attachment rate with an interchange frequency $\beta'$

\[ \beta' = \frac{x}{a_o^2} \left( \frac{2 D_A D_B}{D_A + D_B} \right) \text{ for } x = C_A \left( \frac{A_S}{a_o^2} \right) \]

where $x$ is the number of atoms jumping a jump distance $a_o$ and the subscripts on the diffusivity $D$ represent solute $A$ and solvent $B$. The number of atoms jumping can be evaluated from the surface concentration $C_A$, the interface area $A_S$, and the area per atom. A key finding for multi-component systems is that the rate controlling step for linked flux evaluations is replacement of shell atoms of the controlling species and not the interfacial jump frequency. Thus solute partitioning is critical to understanding nucleation delays.

Unfortunately, classical theory does not include a mechanism whereby melt convection influences the thermodynamics or kinetics of nucleation. Convective solute mass transfer does not significantly enhance diffusivity. For diffusive transport alone the flux may be estimated as

\[ J = D \frac{\partial C}{\partial x} = D \frac{C_c (1-k)}{\Omega a_o} \]
where \( J \) is the atomic flux to the cluster interface, \( D \) is the diffusivity, \( C_L \) the concentration of the key chemical species in the liquid, \( k \) the partitioning coefficient, \( \Omega \) the atomic volume, and \( a_o \) the jump distance. Similarly for convective mass flux in a velocity field with average flow \( V \),

\[
J = \frac{V}{\Omega}
\]  

(7)

Using typical values for each property, convection contributes on the order of only an additional 30% to the total system flux and thus diffusive transport will always dominate. Thus, the role of convection is not to influence nucleation kinetics but rather it influences heterogeneous site development. The delay is thus comprised of two parts – the time to develop a nucleation site and, once the site exists, the time to grow a critical nucleus. Since dendrite fracture is not possible [20] and fragmentation is too slow [21], dendrite collision is the preferred site development mechanism [22].

Three crucial attributes are needed in order to accurately assess the influence of convection on phase selection. First, a single sample must be used for all testing. This ensures that chemical composition is constant and the influence of trace elements, such as oxygen which significantly influences thermophysical properties, is precluded. Second, multiple runs must be achieved at different convection conditions, preferably at a single undercooling. Third, the thermophysical properties of the sample must be known in order to provide accurate model predictions. Note that two models rely on these properties. Magnetohydrodynamic flow modelling must be used to understand and control flow conditions within the droplets [23] during the experiment. Later, solidification models require accurate thermophysical properties in order to track development of the metastable mushy-zone [3] and subsequent stable phase nucleation.

5. The NASA ESL facility for ground-based levitation testing

NASA operates an Electrostatic Levitation facility (ESL) at Marshall Space Flight Center (MSFC) in Huntsville AL. This facility provides critical ground-based thermophysical property measurement capability. Of particular importance to the LODESTARS and ELFSTONE projects is the ability to levitate, melt, undercool and test samples to obtain measurements of surface tension, viscosity and density as a function of temperature and composition [24]. Phase selection studies are also carried out in the absence of convection since the melt is quiescent under electrostatic levitation conditions. This baseline data set is used to anchor space results.

Figure 3 shows a comparison between electrostatic and electromagnetic phase selection test results.

Figure 3. Comparing the nucleation delay times under conditions characterized by no flow (ESL), low flow (\( \mu G \) –EML) and high flow (GB-EML) for a ternary steel alloy.

Figure 4. Nucleation stimulation creates surface forces which influence nucleation delay times even under no flow (ESL) conditions. Triggering must thus be avoided.
Nucleation delays are an order of magnitude slower with no induced flow as compared to results at high turbulent flow. Laminar flow tests during a previous space mission [25] show intermediate results. Ground-based results were obtained by spontaneous heterogeneous nucleation from the melt while the space results were obtained using a nucleation trigger to select the desired undercooling. Figure 4 shows that use of the nucleation stimulation trigger influences the delay time in ESL tests, most probably due to surface deformation with localized melt flow. Triggering is to be avoided in future space missions.

Ground-based ESL testing is enabling in that a wide variety of sample compositions and melt temperatures may be investigated using multiple samples. Unfortunately, all tests must be run without significant melt stirring and thus the influence of convection on phase selection cannot be evaluated using these techniques.

6. The MSL-EML facility for microgravity levitation testing
In ground-based electromagnetic levitation, gravity pulls the sample down into the levitation field causing significant melt convection. Turbulent conditions dominate. By testing in microgravity the need for positioning forces is significantly reduced and stirring may either be minimized or enhanced. Unlike ESL testing, microgravity EML has the ability to access a wide range of melt convection conditions on either side of the laminar/turbulent transition making it the ideal technique for phase selection investigations.

Several attributes are important to attaining the scientific goals of the LODESTARS and ELFSTONE projects. First, ISS microgravity experiment durations are sufficient to allow positioning, melting, undercooling, and phase selection testing on a single sample. Multiple tests may be run in series to provide coverage of the full range of convection conditions. Second, collaborations between the solidification modeling topical team and the thermophysical property evaluation topical team ensure proper experiment control. Recirculation flows within the droplets must be known for each test condition and flow models require accurate properties. Real-time measurement of critical properties, such as viscosity, can be accomplished on the same sample as is used for phase selection tests thus removing uncertainty created by variability introduced by trace alloy elements (such as oxygen content). The three crucial requirements of a single sample, multiple runs at different flow conditions, and know thermophysical properties can only be met using MSL-EML aboard the ISS.

7. Conclusions
The synergy provided by collaboration between the Thermophysical Property and Solidification International Topical Teams organized by ESA and supported by NASA under the LODESTARS and ELFSTONE programs is enabling for evaluating the influence of convection on phase selection. Microgravity testing provides all requirements necessary to provide for controlled convective conditions unattainable in any other environment. Results of these projects will provide new insight toward microstructural control using computerized simulation of solidification phenomena occurring in the mushy-zone for two dramatically different classes of phase transitions.

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