Fluid-Flow Effects on Phase Selection and Nucleation in Undercooled Liquid Metals

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Abstract. Fluid flow can have a profound effect on phase selection and nucleation in undercooled liquid metals.

In phase selection experiments, the sample does not solidify directly to the thermodynamically stable phase, but instead first forms a metastable phase, then transforms to the stable phase after some delay. Previous experiments and modeling on phase selection in near-eutectic Fe-Cr-Ni stainless steels have shown that the lifetime of the metastable phase is limited by the incubation time for formation of a critical nucleus of the stable phase, and that for some conditions, fluid flow can change that incubation time by an order of magnitude or more. New microgravity experiments in this area will be performed on new materials, including peritectic alloys, in the Materials Science Laboratory Electromagnetic Levitator (MSL-EML) as a part of projects PARSEC and THERMOLAB. The models that predict the effect of fluid flow on phase selection will be extended to these new experiments.

In another class of experiments, nucleation in quasicrystal- and glass-forming alloys, testing a new theory on nucleation kinetics requires control of the shear rate in fluid flow to prevent interference of the solute fields around the sub-critical nuclei. These theories will be tested in microgravity using the MSL-EML under the projects ICOPROSOL and THERMOLAB.

1. Introduction
Fluid flow has been shown to have an effect on a variety of solidification and nucleation processes. Effects which have been observed include distortion of solutal and thermal diffusion fields, gross fluid flow leading to macrosegregation, and even mechanical effects such as the bending or breaking of dendrites.

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Two groups of experiments are discussed in this paper. Each group is being developed by international teams assembled under the European Space Agency’s announcements of opportunity. The first group of experiments deals with phase selection in metals. Eutectic alloys including Fe-Cr-Ni alloys are being studied under the European Thermolab project, with the American partners funded under NASA’s project LODESTARS. Related experiments on peritectic alloys including Fe-Co and Ti-Al-Ta are under ESA’s PARSEC and NASA’s ELFSTONE. These projects are described in more detail in [1].

The second group of experiments discussed here is looking at nucleation in quasicrystal- and glass-forming alloys. This group also includes samples under ESA’s Thermolab projects, and ESA’s ICOPROSOL / NASA’s QUASI projects. These experiments are described in more detail in [2].

2. Phase Selection in Eutectic and Peritectic Alloys

In phase selection experiments, the sample does not solidify directly to the thermodynamically stable phase, but instead first forms a metastable phase, then transforms to the stable phase after some delay. Previous experiments and modeling on phase selection in near-eutectic Fe-Cr-Ni stainless steels have shown that the lifetime of the metastable phase is limited by the incubation time for formation of a critical nucleus of the stable phase, and that for some conditions, that incubation time may change by an order of magnitude or more (Fig. 1). All of the experiments shown in Fig. 1 had spontaneous nucleation.

Figure 1. Lifetime of the metastable phase (Delay Time) vs. undercooling for steel samples processed in 1-g in Electromagnetic Levitation (EML) and Electrostatic Levitation (ESL) [3].

Fair, et al., investigated a number of potential causes of this change in incubation time [4]. They concluded that none of those mechanisms was a plausible explanation for the observed behavior of the
samples. One hypothesis that remained was examined by Hanlon, et al., [5]: that flow in the liquid part of the sample was causing deflection of the dendrite arrays sufficient to cause collision of the secondary arms, leading to crevice nucleation (Fig. 2). They used computational fluid dynamics to determine the drag force on the tips of the primary arms (Fig. 3), and then evaluated analytical models to make quantitative predictions for different mechanisms of deflection including creep and elastic and plastic bending. They determined that elastic deformation of the growing dendrites would be sufficient to cause collision when the dendrites reached a critical length, and determined the time to reach that length from measurements of the growth velocity [6]. The resulting time to collision predicted by the model matched the experimental delay time within the scatter of the experimental data [5].

![Figure 2. Hypothesized mechanism of nucleation of the stable phase due to the influence of fluid flow on the growing metastable dendrites [5].](image)

This model requires a significant amount of information about the microstructure of the metastable phase, including diameters of the primary arms of the dendrites and spacing of the secondary arms. This information is collected from micrographs of samples quenched between the formation of the stable and metastable phases, e.g. [7]. The micrographs of the quenched structure show that at a time within fractions of a millisecond before the nucleation of the stable phase, the dendrites have the approximately parallel arrangement assumed in the model.

The input data necessary for the models were available for two other compositions, one with a very low thermodynamic driving force for transformation (the difference in free energy between the metastable and stable phases), and one with an intermediate driving force. The sample with an intermediate driving force showed fair agreement with the model, indicating that the same mechanism is plausible for that alloy as well. For the smallest driving force, there was no agreement, indicating that this mechanism is not active. For a transformation with a small driving force, it is plausible that the transformation might not happen immediately on establishment of the crevice.
For application of Hanlon’s model to the new eutectic and peritectic systems to be tested under THERMOLAB/LODESTARS and PARSEC/ELFSTONE, respectively, a number of data are required. These include:

- Properties of the liquid including density, viscosity, electrical conductivity. These properties will be measured on the flight samples as a part of the experiments in MSL-EML.
- Properties of the solid at its melting point, including elastic modulus and yield strength. The delay time predicted by the model is only weakly influenced by these properties, so extrapolations from lower temperatures will be used.
- Properties of the metastable dendrite array, including primary and secondary arm spacing and the diameter of the primary arms. These are the most difficult to obtain of all the needed data. Hanlon used micrographs by Kosecki [7] of samples quenched in the metastable state. Replicating this measurement is an important part of the ground support program for these experiments.

Once these data are obtained, the chain of models will allow determination of the range of convection where fluid-flow effects are expected to be important, and from there, the parameters needed to test for the presence of this mechanism in phase selection in the new alloys.
3. Nucleation in Undercooled Metals

The coupled-flux theory of nucleation has been well established for oxide glasses [8]. Testing this theory in metals is experimentally very difficult, in part because convection tends to distort the diffusion profiles around the subcritical nuclei since the viscosity is many orders of magnitude smaller than in the silicates. Microgravity experiments provide the possibility of removing the convective distortion, but models are needed to quantify convective flow and relate it to controllable experimental parameters.

The simple model for the relevant phenomena is depicted in Fig. 4. Two nuclei, each surrounded by its diffusion field, are carried along with the moving fluid. However, since the velocity of the fluid cannot be uniform throughout an EML droplet, nuclei on nearby streamlines move at different velocities. If the centers of the nuclei are close enough in the direction normal to the flow, then the diffusion fields will eventually interact. If the centers are farther apart than one diffusion field diameter, then the nuclei will pass without interacting.

\[
\Delta V = \left( \frac{\partial V}{\partial x} \right) (2r_D)
\]

\[
t_{\text{collision}} \approx \frac{d}{\Delta V} \gg t_{\text{nucleation}}
\]

\[
\frac{\partial V}{\partial x} < 0.05 \text{sec}^{-1}
\]

Figure 4. Model for the effect of fluid flow on the diffusion fields around subcritical nuclei [9].

The case illustrated in Fig. 4 provides the shortest possible time before the nuclei interact. Knowing the dimensions of the diffusion field and the number density of nuclei, it is possible to calculate a constraint on the allowable shear rate to prevent collisions during the time of the experiment. For a cluster separation \(d\) of \(1 - 0.1 \mu m\), a diffusion fields of radius \(r_D\) of about 10 nm, and a cooling rate of about \(10 \, ^{\circ}C \, s^{-1}\), the result is that the velocity is not explicitly constrained, but the shear rate must be less than 0.05/s throughout the drop [9].

Other effects must also be considered. First, the diffusivity of momentum (kinematic viscosity) is perhaps four orders of magnitude greater than the diffusivity of solute in these alloys, so momentum transfer will happen much faster and at much longer range than the diffusion fields around the nuclei.
However, the nuclei are very small, only nanometers in diameter, so the Stokes number is very close to zero (of the order $10^{-13}$). That means that the nuclei follow the path of the surrounding fluid very precisely, and do not distort the streamlines. Accordingly, each differential volume of fluid behaves the same whether the next differential volume is liquid or crystalline, and the nuclei are transported as in the model in Fig. 4.

Second, the shear in the fluid affects each nucleus directly. Because of fluid drag, the top of each nucleus in Figure 4 must move faster than the center, and the bottom must move slower, so each nucleus must rotate. The rotation rate in radians per second must approximately equal to the shear rate in inverse seconds. Rotating spheres in a flow experience lift due to the Magnus effect, which causes baseballs and tennis balls to curve. The lift due to the Magnus effect is proportional to the cross product of the vorticity and the relative velocity between the sphere and the fluid. In this case, as already established, the relative velocity is zero, so the Magnus forces are also zero.

Finally, the rotation itself will cause some distortion of the fluid flow as the nucleus rotates like a centrifugal pump. This effect will cause an additional radial outflow in the plane of Figure 4, and a compensating inflow toward the nuclei from planes above and below the figure. However, the rotation rate is very low, of the order 0.05 rad/sec, and the impeller radius is also very small, of the order nanometers. The resulting flow is too small to have a significant effect on the diffusion fields, again confirming the simple picture in Figure 4.

Finally, now that the constraints on the flow field have been established, magnetohydrodynamic models are used to determine the corresponding constraints on the operational parameters such as coil currents in the MSL-EML. These models use properties measured in the ground support program, and will be updated with properties determined on the flight samples as a part of the experimental program.

4. Conclusions
Fluid flow is important in both classes of experiments described above, but through different mechanisms. In one case, the shear rate in the fluid must be kept everywhere below a particular value to test a theory about nucleation of crystals in a liquid, while in the other the fluid’s velocity must be varied within a range to test a theory about nucleation of the stable phase in a mixture of liquid and metastable solid. Computational models of the magnetohydrodynamic flows in electromagnetically levitated droplets, combined with accurate thermophysical properties, allow the use of flow as an experimental parameter.

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