Experiments on Nucleation in Different Flow Regimes

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Introduction

The vast majority of metallic engineering materials are solidified from the liquid phase. Understanding the solidification process is essential to control microstructure, which in turn, determines the properties of materials. The genesis of solidification is nucleation, where the first stable solid forms from the liquid phase. Nucleation kinetics determine the degree of undercooling and phase selection. As such, it is important to understand nucleation phenomena in order to control solidification or glass formation in metals and alloys.

Early experiments in nucleation kinetics were accomplished by droplet dispersion methods [1-6]. Dilitometry was used by Turnbull and others, and more recently differential thermal analysis and differential scanning calorimetry have been used for kinetic studies. These techniques have enjoyed success; however, there are difficulties with these experiments. Since materials are dispersed in a medium, the character of the emulsion/metal interface affects the nucleation behavior. Statistics are derived from the large number of particles observed in a single experiment, but dispersions have a finite size distribution which adds to the uncertainty of the kinetic determinations. Even though temperature can be controlled quite well before the onset of nucleation, the release of the latent heat of fusion during nucleation of particles complicates the assumption of isothermality during these experiments.

Containerless processing has enabled another approach to the study of nucleation kinetics [7]. With levitation techniques it is possible to undercool one sample to nucleation repeatedly in a controlled manner, such that the statistics of the nucleation process can be derived from multiple experiments on a single sample. The authors have fully developed the analysis of nucleation experiments on single samples following the suggestions of Skripov [8]. The advantage of these experiments is that the samples are directly observable. The nucleation temperature can be measured by noncontact optical pyrometry, the mass of the sample is known, and post processing analysis can be conducted on the sample. The disadvantages are that temperature measurement must have exceptionally high precision, and it is not possible to isolate specific heterogeneous sites as in droplet dispersions.

Experimental Method

Levitation processing of refractory materials in ultra high vacuum provides an avenue to conduct kinetic studies on single samples. Two experimental methods have been identified where ultra high vacuum experiments are possible; electrostatic levitation in ground based experiments and electromagnetic processing in low earth orbit on TEMPUS [9]. Such experiments, reported here, were conducted on zirconium. Liquid zirconium is an excellent solvent and has a high solubility for contaminants contained in the bulk material as well as those contaminants found in the vacuum environment. Oxides, nitrides, and carbides do not exist in the melt, and do not form on the surface of molten zirconium, for the materials and vacuum levels used in this study.

Ground based experiments with electrostatic levitation have shown that the statistical nucleation kinetic experiments are viable and yield results which are consistent with classical nucleation theory [9]. The advantage of low earth orbit experiments is the ability to vary the flow conditions in the liquid prior to nucleation. The purpose of nucleation experiments in TEMPUS was to examine the effects of fluid flow on nucleation.

The primary evidence for a change in nucleation behavior is a shift in the mean undercooling. It is not necessary to know the functional form of the nucleation rate equation, or the operative mechanism to make the comparison of nucleation behavior under two different flow conditions. Simply stated, if the nucleation rate is different for two experimental conditions, then the parent distribution of nucleation events is different and the mean undercooling is different.

Null hypothesis testing is used to determine if the difference in means of two samples reflects a significant difference in the means of parent distributions for two experimental conditions. Two sets of data (A and B) can be compared by analysis of means using the null hypothesis.

The null hypothesis (H_0) is:

The mean nucleation temperature in experiment A and experiment B are identical.

and, the alternate hypothesis (H_1) is:

The mean nucleation temperature in experiment A and experiment B are different.

If H_0 is rejected and H_1 supported, then the means of the parent distributions are different and therefore the nucleation rate as a function of temperature is different.

The central limit theorem states that the means of samples from a population will be distributed normally, even if the population is not normally distributed. Nucleation temperature distributions, particularly those at low activation energies, are not normally distributed. However, in invoking the central limit theorem, no assumptions about the underlying distributions are necessary, and the means of two samples can be compared by using Student's "t" distribution [10].

Results and Conclusions

Statistical distributions of undercoolings were generated in "free cooling" experiments on TEMPUS. During free cooling the heater power is set to the lowest value, and the power input to the sample comes from the positioning field. One sample was repeatedly melted and cooled to freezing, holding all experimental variables constant except for the positioner power settings on cooling. Two different power supply settings were used; the lowest positioner power capable of stable positioning of the sample, and a high positioner power. The pure radiation cooling rate for this sample is $53Ks^{-1}$. At the low positioner power the cooling rate was $50Ks^{-1}$, and at the high positioner power the cooling rate was $48Ks^{-1}$. Fluid flow calculations for the lower positioner power indicate the undercooled liquid is in the laminar flow regime with flows of approximately 4 cm s^{-1} and Reynolds numbers of about 200[11]. Modeling is continuing to characterize the flow regime corresponding to the higher positioner power which is know to be greater than the low

power. The experiments were interspersed to minimize any effect of sample history on the comparison.

The distributions of undercoolings for these experiments and the nucleation kinetic fits are shown in figure 1. A t-test for mean undercooling at the 95% confidence level supports the null hypothesis and rejects the alternate hypothesis. These experiments revealed there is no significant change in the nucleation behavior in the range of flow conditions tested.

The kinetic determinations made from the distributions, assuming the classical nucleation expression [12] are given in table I. These kinetic determinations are consistent with ground based experiments on zirconium using the electrostatic levitator. The kinetic values are similar to those for arc melted samples, and are lower than the maximum values (ΔTmean=348K, $K_v=10^{43}$, ΔG^*=88kT) obtained on a machined sample in the electrostatic levitator. The kinetic determinations are believed to be lower because of the temperature measurement uncertainty caused by sample translations on MSL-1. The maximum mean undercoolings from MSL-1 scale to the maximum achieved in the ESL if volume and cooling rate are considered.

Other experiments were conducted to determine the surface tension and viscosity of the undercooled melt [13], and to examine the heat capacity by noncontact modulation calorimetry [14]. To accomplish these experiments in the undercooled melt, the heater power was used to hold liquid samples at the desired temperature and pulsing or modulation of the heater was used to excite surface oscillations or to modulate the temperature of the sample. Experiments at low temperatures (and heater powers) were followed by free cooling to the nucleation temperature, which, in all cases was within the bounds of the distributions in the previous experiments. In experiments near the melting temperature, at heater voltages above 220 V, the undercooling of the samples was significantly limited as shown in figure 2. At 220 V heater the flows are estimated to be 50 cm s^{-1}. Initial analysis by Hyers and Trapaga indicates that at these flows the dynamic pressure is equal to the static pressure in the samples, a condition which is known to cause cavitation in fluid flows [15]. The collapse of cavitation bubbles creates sufficient pressures to raise the melting point of the material through the Clapyeron equation such that nucleation of the solid occurs [16-18].

Additional evidence of nucleation by cavitation can be found in the modulation experiments. A compilation of specific heat/total hemispherical emissivity (Cp/ϵ) determinations from the drop tube, electrostatic levitator and TEMPUS is shown in figure 3. The drop tube data was derived by measuring the release temperature of Zr pendant drops, the free fall time to recalescence in vacuum, and the nucleation temperature. In 135 experiments with masses around 0.23 g, the average ratio of specific heat to total hemispherical emissivity was 1.57 with a one sigma standard deviation of 0.03. In the electrostatic levitator, 332 cooling curves (four samples, mass range from 0.013 to 0.057 g) were evaluated by a sliding boxcar fit of the cooling curves to the radiation cooling equation solving for Cp/ϵ. The average value over the temperature range was 1.54 ± 0.12 (1σ). The TEMPUS modulation Cp/ϵ data falls within the bounds of these other determinations except for the experiment at the melting temperature. This determination is apparently 13-15% higher than the rest of the data. Other determinations indicate that there is no temperature dependence of Cp/ϵ in the measured range and do not support the findings of the TEMPUS

modulation experiment at the melting temperature. In essence, the melting temperature data showed a smaller modulation in temperature for the applied power modulation. The temperature modulations in this experiment were 10K above below the melting temperature at a frequency of 0.1Hz. A cyclic phase transformation including nucleation by cavitation and subsequent remelting provides a heat source during cooling and a heat sink during melting which explains the decrease in the temperature modulation around the melting point. This explanation is consistent with the above fluid flow calculations.

These experiments indicate that fluid flow has no effect on nucleation until the cavitation phenomenon occurs, and that cavitation induced nucleation is responsible for limiting bulk undercooling in the higher flow regimes.

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Table I: Results of kinetic determinations of nucleation distributions from MSL-1R. The Classical Turnbull-Fisher expression was used to fit the distributions.

Positioner Power	Mean Undercooling $\Delta T_{avg} \pm 1\sigma$ (K)	$\log K_v$ ($\sigma \approx 3.0$)	ΔG^* (kT) ($\sigma \approx 7.0$)
Low	333.8 ± 4.8	29	62
High	334.7 ± 3.2	34	72

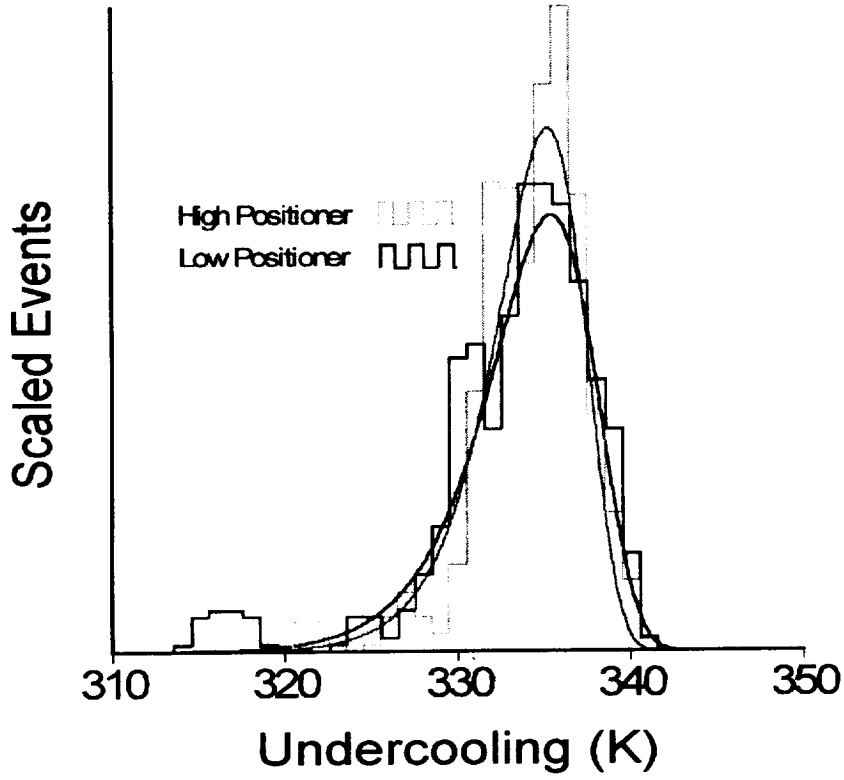

Figure 1: Two distributions from "free cooling" experiments on MSL-1R. The Low Positioner distribution is in the laminar flow regime and the High Positioner is believed to be in a transitional flow regime.

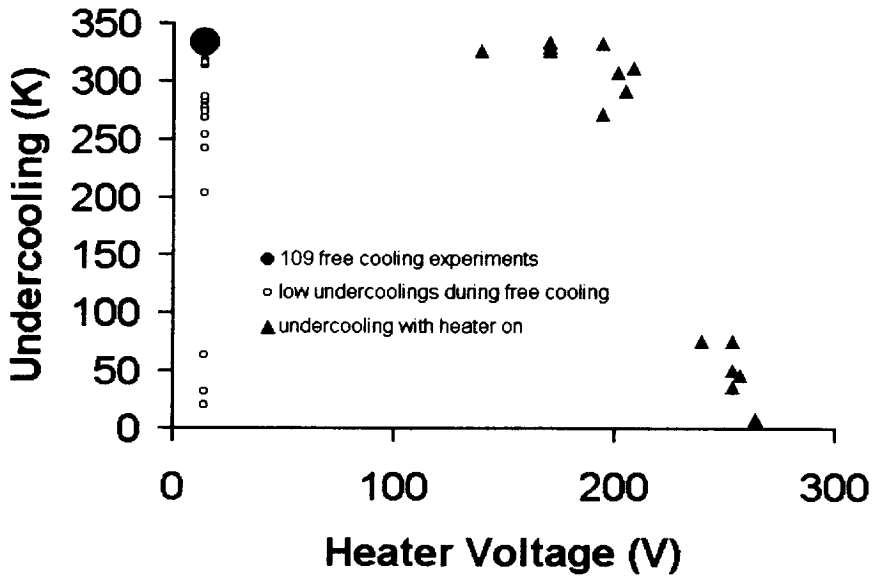

Figure 2: All zirconium undercoolings from two samples are compiled in this graph as a function of heater voltage applied during the cycle. Both distributions in figure 1 are contained in the large circle at the upper left. Samples processed above 220 V heater would not undercool to the same level as those cooled with less heater voltage applied.

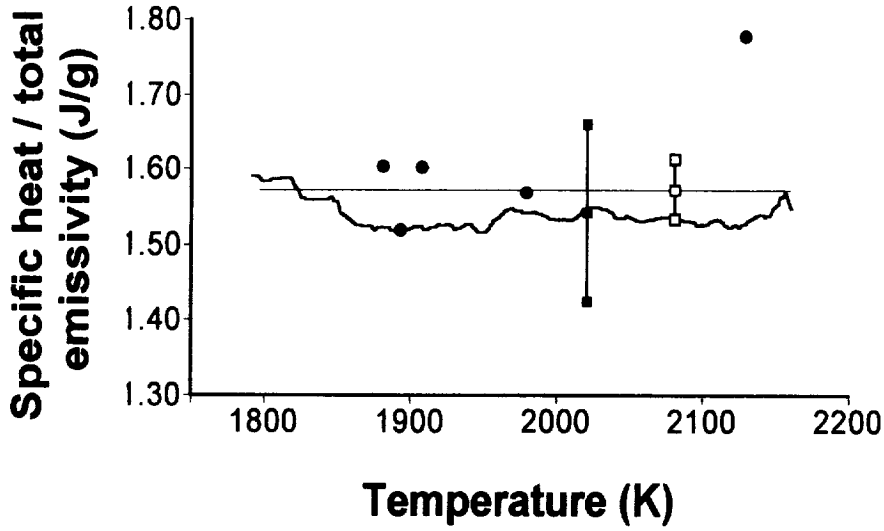

Figure 3: The ESL data as a function of temperature is plotted as the thick black line. The average ESL data over the temperature range is represented with filled squares. The drop tube data temperature range is represented with a thin straight line and the mean and one sigma points as open squares. The modulation calorimetry results from TEMPUS are given as filled circles.