Study of the Influence of Inducing Nucleation on the Performance of the Freezing Temperature Plateau of Metal Fixed-Point Cells

Speaker: Rong Ding
Fluke Corp. - Hart Scientific Division
799 East Utah Valley Drive
American Fork, Utah 84003-9775, USA
Phone: (801) 763-1600; Fax: (801) 763-1010
E-mail: rong.ding@hartscientific.com

Authors: R. Ding, M.J. Zhao, D. Cabana, D. Chen, R. Walker

Abstract

Experimental research was carried out to investigate the influence of the technique of inducing nucleation on the performance of the temperature plateau during the realization of freezing points of metal fixed-point cells. Different induction techniques were studied in the experiments. The experimental results show that the induction methods and the induction time significantly affect the performance of the freezing temperature plateau, especially at the beginning of freezing. Insufficient induction removes too little of the latent heat released by the start of the freeze and causes delayed settling at the beginning of the plateau. The induction method, induction duration, and the furnace maintenance temperature should be carefully chosen based on the characteristics of the particular fixed-point cell in order to provide sufficient cooling for nucleation and obtain the ideal freezing temperature plateau. A simple theoretical analysis shows that the freezing plateau duration is inversely proportional to the temperature difference between the furnace maintenance temperature and the freezing-point temperature. The freezing rate along the radius direction increases linearly with the temperature, and varies during the freezing process. The analytical results agree well with the experimental results.

1. Introduction

The performance of the freezing plateau of fixed-point cells depends on a few factors, e.g. impurities in the cells, the method of inducing nucleation, and the furnace maintenance temperature. Extensive studies have been carried out in the past half century to investigate the influence of these factors on the freezing plateau [1-10]. Different induction methods have been studied in order to achieve a long constant freezing temperature plateau. For metals with smaller natural supercool, such as indium, zinc, and silver, the induction method by withdrawing the thermometer from the re-entrant well, cooling it down outside the furnace for a few minutes, and then reinserting it into the well, or inserting a quartz glass rod for a few minutes [10], can form a mantle of the frozen metal around the well [1,3]. For metals with larger natural supercool, such as gallium, tin and aluminum, the outer nucleation method, which removes the crucible from the furnace for a few minutes [5] or blows cold nitrogen or argon gas over the outside of the cell [6], can be used to trigger nucleation around the crucible wall for freezing.

When nucleation is induced in the re-entrant well by using a thermometer or a quartz glass rod, a mantle of frozen metal can be formed around the re-entrant well with the thickness of a few millimeters. The mantle remains during the whole freezing process because there is little heat loss through the thermometer sheath. Freezing continues slowly in a cylindrical shell from the crucible walls to the center of the cell because of the heat transfer from the metal sample to the furnace. Typical rates for the advance of the solid-liquid boundary are 2 to 5 mm per hour [4]. In order to get a long and constant freezing plateau, all the parameters should be controlled carefully, e.g. the induction time, the cooling rate, and the furnace maintenance temperature.

In this paper, the influence of the induction methods, induction duration, and the furnace maintenance temperature on the performance of the freezing plateau of sealed metal fixed-point cells (including tin, zinc, aluminum, and silver cells) is investigated, and the experimental results are discussed. A simple theoretical analysis about the length of the freezing plateau and the freezing rate is made, and the analytical results are compared with experimental observations.

2. Experimental methods and results

In order to investigate the influence of inducing nucleation methods on the performance of freezing plateaus of fixed-point cells, the different factors were studied, including the induction method, the induction duration, and the furnace maintenance temperature. These parameters affect the performance of the freezing plateau in different degrees.

In this study, two furnaces were used to maintain the fixed point cells: Fluke Hart Scientific sodium heat-pipe furnace (model 9115) for the silver cell and Fluke Hart Scientific three-zone freeze-point furnace (model 9114) for other cells. Standard platinum resistance thermometers (SPRTs) were used to measure temperatures in the cells: Fluke Hart Scientific models 5681 and 5683 for the tin, zinc and aluminum cells, and Fluke Hart Scientific model 5684 high temperature SPRT for the silver cell. Three resistance bridges were used to measure the resistances of the SPRTs: Guildline DC current comparator model 6675A (accuracy ±0.1ppm), Measurements International DC current comparator model 6010T (accuracy: <±0.05ppm), and ASL F18 AC thermometry bridge (accuracy: <±0.1ppm). Leeds & Northrup 1 ohm DC and Tinsley 10 ohm AC/DC standard resistors were used with the bridges. A triple point of water cell, Fluke Hart Scientific model 5901, with appropriate maintenance bath (Fluke Hart Scientific model 7312), provided the temperature comparison standard.

2.1 Induction methods

Different induction methods were studied and reported in prior research [1-6], including cooling the cell with the thermometer by removing the thermometer from the re-entrant well of the fixed-point cell for a few minutes, temporarily removing the cell from the furnace, inserting a room-temperature quartz glass rod or tube into the re-entrant well, and flowing cool nitrogen or argon gas around the outside of the cell. The appropriate induction method should be chosen according to the supercool characteristics of the different metals in fixed-point cells.

In this study, two different methods of inducing nucleation were tried. Room-temperature quartz glass tubes and rods were used in tin, zinc, aluminum, and silver fixed-point cells. And compressed air was also used in tin cells. Differences in results between these two induction methods will be compared and discussed.

An experiment to compare the induction results using a quartz glass tube or rod with a sealed fused-silica-cased zinc fixed-point cell (Fluke Hart Scientific model Zn-5906) was carried out. Initially, the furnace temperature was set 4K above the freezing temperature, and the cell's temperature was allowed to stabilize for at least two hours. To begin the freeze, the furnace was set to slowly cool down to 2K below the theoretical freezing temperature at the scan rate of 0.1 K/minute. An SPRT in the cell monitors its temperature. As soon as recalescence occurs, recognized by a sudden rise in temperature, the SPRT is removed and the first cool quartz glass tube is inserted into the well and left for two minutes. Then it is removed and the second cool quartz glass tube is inserted for three minutes. After induction, the furnace's temperature is raised to 0.4 K below the freezing temperature and maintained for the duration of the freezing plateau.

Figure 1 shows the resulting freezing temperature plateau. The figure shows that the front end of the freezing temperature curve is falling at the beginning of the freeze until it becomes flat within about 30 minutes. The duration of the freezing plateau lasts over 30 hours before it drops off. The decreasing temperature at the beginning of the freeze is a result of the temperature rising past the plateau temperature during recalescence because too little of the latent heat released during induction was drawn away. The remaining latent heat exceeds the amount which is required to maintain the dynamic balance between the heat loss from the thermometer in the re-entrant well and the latent heat released in the continuous freezing. It raises the temperature of the re-

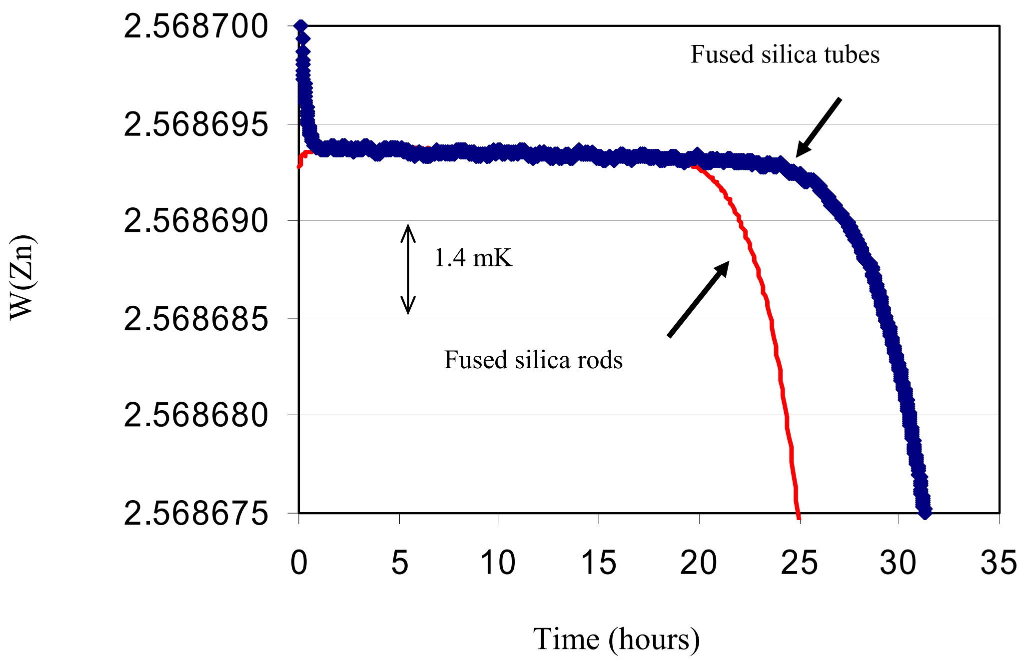

Figure 1. Zinc freezing plateaus using two different induction methods.

entrant well above the plateau temperature. Then when a room-temperature platinum resistance thermometer is inserted into the re-entrant well, this quickly draws away the excessive heat and the temperature drops down to the plateau. If more heat is removed during induction, by keeping the quartz glass tube in the well longer or using solid rods instead, the heat will equilibrate sooner, and the temperature overshoot at the beginning of the plateau can be avoided.

In another test, two room-temperature quartz glass rods were used to induce nucleation. The first quartz glass rod was inserted into the well for two minutes, and then the second one was inserted for three minutes. The resulting freezing temperature plateau is also shown in Figure 1. It can be seen that the falling temperature at the beginning of the plateau has disappeared. The duration of the plateau is about 20 hours, which is a little shorter than that for the quartz glass tube induction, but still adequate for a day's work.

Previous studies have shown that for metals with a large natural supercool, the nucleation can be induced by flowing argon or nitrogen around the crucibles [6], temporarily raising the cell to the mouth of the furnace [1], or even temporarily removing the cell from the furnace and placing into another furnace until recalescence occurs [5]. All of these induction methods provide sufficient cooling for trigging nucleation and releasing enough latent heat to raise the cell's temperature to the freezing point. In this paper, induction techniques are studied for two different types of tin fixed-point cells. One type is the classic sealed fused-silica-cased tin cell (Fluke Hart Scientific model Sn-5905). The second is a sealed metal-cased tin fixed-point cell (Fluke Hart Scientific model Sn-5945).

For the fused-silica tin cell, nucleation was induced by passing room-temperature compressed air around the cell when the temperature drops to the freezing point from a temperature of 4 K above the freezing point. After recalescence, the air flow was immediately stopped and a quartz glass tube was inserted into the re-entrant well and kept there for three minutes. Then a second

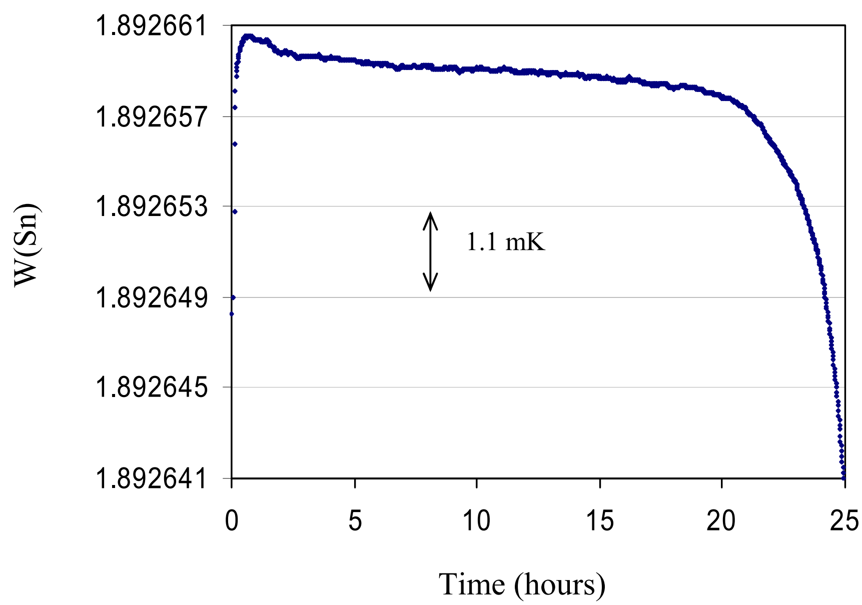

Figure 2. The freezing plateau of a tin cell using compressed air to induce nucleation.

quartz glass tube was inserted for another three minutes. The resulting freezing plateau is shown in Figure 2. The duration of the plateau for 2 mK tolerance is more than 20 hours. At the beginning of the freezing plateau, there is a slight overshoot. The cause of this is the same as that for the zinc cell with quartz glass tube induction.

For the metal-cased tin cell, two different induction methods were tested. The first method was the same as with the fused-silica tin cell, using both cool compressed air and quartz glass tubes. The second method was to insert two quartz glass rods into the well sequentially without flowing compressed air. Each fused silica rod remained in the well for two minutes. The results are shown in Figure 3. The plateau duration using the forced air was 13 hours before a 2 mK fall-off. In contrast, the plateau duration using only the quartz glass rods was about 23 hours, obviously much longer. The conclusion is that for a metal-cased tin cell, it is best not to apply compressed air or other gas, such as nitrogen or argon, to cool down the crucible for outer induction. This is because heat transfer from the cell to the furnace is greater for the metal-cased cell. The gas removes too much heat, causing excessive solidification, which results in a short freezing plateau.

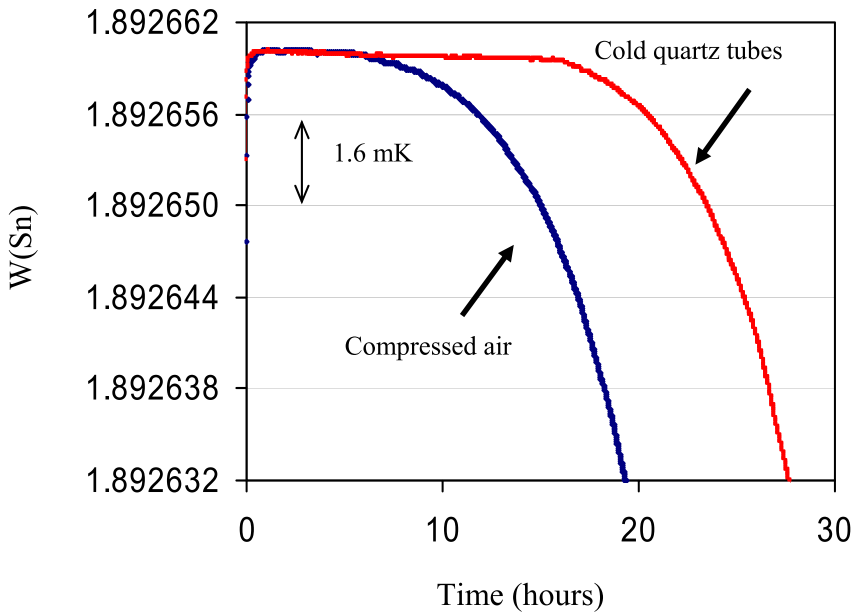

Figure 3. Freezing plateaus of the sealed metal-cased tin cell comparing induction methods.

2.2 Induction duration

The induction duration has an important influence on the performance of the freezing temperature plateau. Longer duration of induction causes more extensive solidification which shortens the duration of the freezing plateau. However, too short induction time may result in failure to form a frozen mantle around the thermometer well, and a proper freezing plateau might not be obtained. Figure 4, plot A, shows the freezing plateau of a sealed fused-silica-shelled silver cell obtained by inserting a quartz glass tube into the re-entrant well for 2 minutes to induce nucleation as soon as the recalescence occurs. The furnace temperature is kept at 0.3 K below the freezing temperature. It can be seen that there is overshoot at the beginning of the plateau because of insufficient induction as explained in section 2.1. When the induction time is increased to 3 minutes (Figure 4, plot B), the freezing plateau is normal and overshoot at the beginning is avoided. The duration of the plateau before a 2 mK fall-off is about 17 hours. If the induction time is increased to 4 minutes (Figure 4, plot C), the plateau duration is only 12 hours. Again, the long induction time removes too much heat and too little metal is left as a liquid.

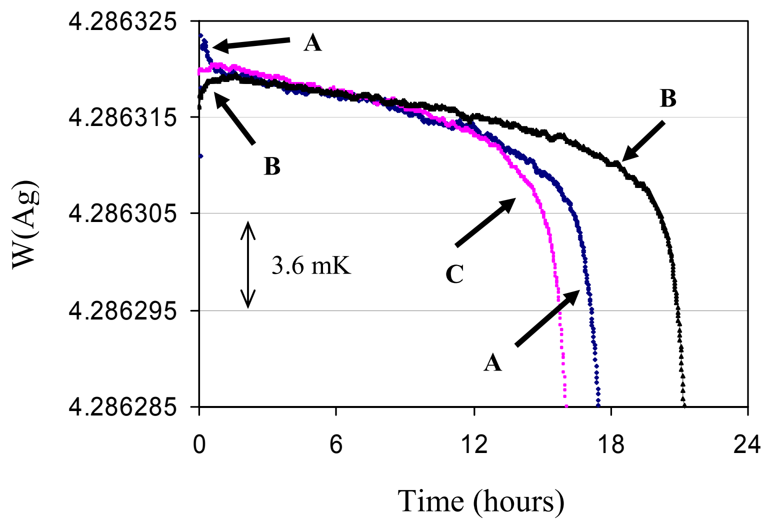

Figure 4. Freezing plateaus of a fused-silica-cased silver cell with different durations of induction (A: 2 minutes, B: 3 minutes, C: 4 minutes).

2.3 Furnace maintenance temperature

During the realization of the freezing plateau, the furnace maintenance temperature should be controlled at an optimal value, which is 0.3 to 1.0 K below the freezing point temperature, in order to produce a long and stable plateau. If the furnace temperature is too low, the solidification process proceeds too quickly, resulting in a short plateau period. If the furnace temperature is too close to the freezing point, e.g. 0.1 to 0.2 K below, the plateau might last a long time, but if the furnace temperature drifts up only 0.2 K, the metal will start to melt again and the freezing plateau will be destroyed.

Figure 5 shows freezing plateaus of another sealed fused-silica-cased silver fixed-point cell at three different furnace temperatures, which are 0.3 K, 0.45 K, and 1.2 K below the freezing point. The induction method was the same for all three. First, the furnace temperature was slowly decreased to 1.5 K below the freezing point at a rate of 0.1 K per minute. Next, one quartz glass tube was inserted into the re-entrant well for three minutes as soon as recalescence occurred. After the tube was withdrawn from the well, the furnace temperature was adjusted to the maintenance temperature, and an SPRT was inserted into the well to start measuring.

It can be seen in Figure 5 that when the furnace maintenance temperature was 1.2 K below the freezing point, the plateau was very short. The duration before a 2 mK drop-off was only about 6 hours. When the furnace temperature was 0.45 K below the freezing point, the plateau duration increased to 14 hours. With the furnace temperature only 0.3 K below the freezing point, the plateau duration was 17 hours.

In the experiments, it was found that the plateau duration of high-temperature fixed-point cells (e.g. aluminum and silver) were more sensitive to the furnace maintenance temperature than those of low-temperature cells (e.g. indium and tin). This is because of the greater effects of convection and radiation at higher temperatures.

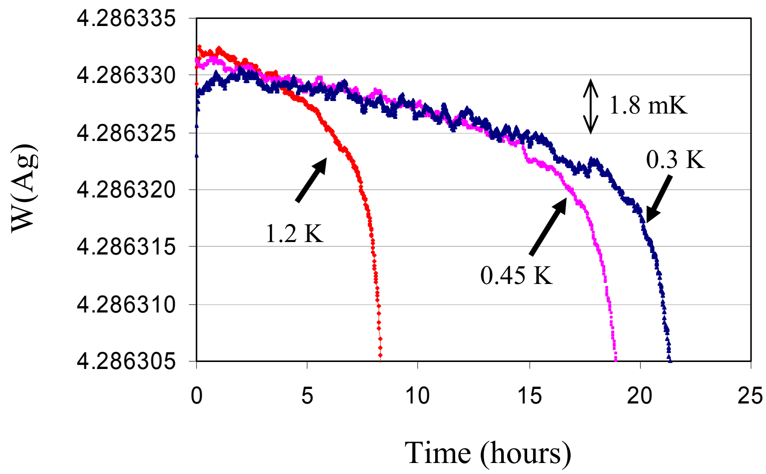

Figure 5. Freezing plateaus of a sealed fused-silica-cased silver fixed-point cell at different furnace temperatures (0.3 K, 0.45 K, and 1.2 K below freeze).

3. Discussion

It is desirable to achieve long, stable freezing plateaus when using fixed-point cells. This helps to minimize measurement uncertainties and provides more time to calibrate thermometers. The quality of the freezing plateau depends on many factors. A simple analysis can be made to analyze the influence of the furnace maintenance temperature on the duration of the freezing plateau. It is assumed that the fixed-point cell is cylindrical, as shown in Figure 6. During the freezing process, the latent heat released because of solidification should be in balance with the heat loss from the outside of the crucible to the furnace. It is assumed that the heat loss through the thermometer in the central well and radiation from the top of the cell are negligible. A simplified equation can be obtained according to the heat balance during the freezing process:

$$\Delta H \cdot dm = k \cdot \frac{\Delta T}{(r_0 - r)} \cdot (2\pi \cdot r_0 \cdot h) \cdot dt \qquad (1)$$

where ΔH is the latent heat (J/kg), dm (kg) the mass of metal solidified during the time dt (s), k (W/m·K) the effective thermal conductivity between the metal sample inside the crucible and the furnace (which includes heat transfer from the metal sample to the graphite crucible, from the crucible to the fused-silica shell, from the fused-silica shell to the cell holder or basket, and from the basket to the inside wall of the furnace), ΔT the difference between the temperature of the molten metal (the freezing temperature of the metal) and the furnace maintenance temperature, r the radius of the solid-liquid boundary, and r_0 the radius of the metal sample.

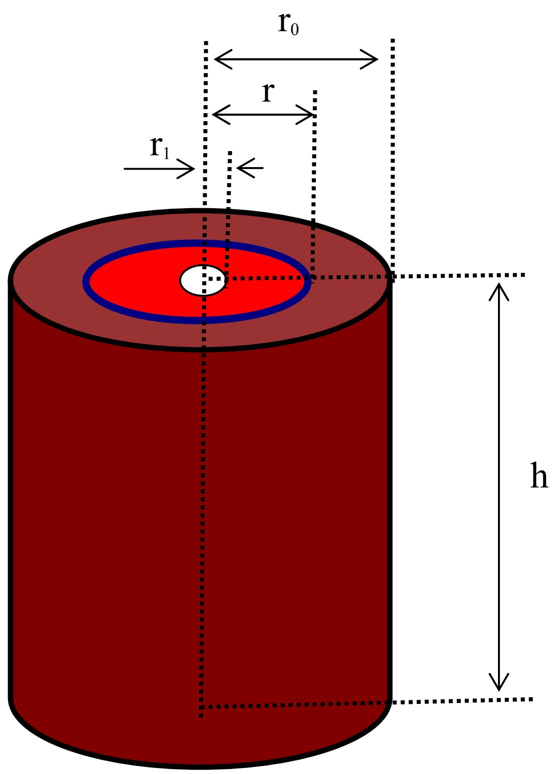

Figure 6. Geometry of the frozen metal inside the crucible.

Equation (1) can be written as follows according to the dynamic heat transfer balance during a time increment dt :

$$\Delta H \cdot \rho \cdot \pi \cdot \left[(r + dr)^2 - r^2 \right] \cdot h = k \cdot \frac{\Delta T}{(r_0 - r)} \cdot (2\pi \cdot r_0 \cdot h) \cdot dt \qquad (2)$$

where ρ (kg/m^3) is the density of the metal, dr the change in radius of the frozen metal during time interval dt, and h the height of the metal sample. Omitting the vanishingly small term $(dr)^2$ and assuming the furnace maintenance temperature remains unchanged during the entire freezing process, the following equation can be obtained by integrating both sides of equation (2):

$$\int_{r_0}^{r_1} \Delta H \cdot \rho \cdot (r_0 r - r^2) \cdot dr = \int_0^t k \cdot \Delta T \cdot r_0 \cdot dt \qquad (3)$$

Here r_1 is the outer radius of the re-entrant well and t the total freezing time. The relationship of the temperature difference and the total freezing time can be obtained as:

$$\Delta T \cdot t = \frac{\Delta H \cdot \rho \cdot \left(r_0^3 - 3r_0 \cdot r_1^2 + 2r_1^3\right)}{6k \cdot r_0} \tag{4}$$

For a designated fixed-point cell, the latent heat ΔH, the density of the metal ρ, and the radii r_0 and r_1 of the cell can be considered constant. The effective thermal conductivity k can also be considered nearly constant given a particular furnace and fixed-point cell design.

It can be seen from equation (4) that the total freezing time is inversely proportional to the temperature difference when other parameters are fixed. This agrees well with the experimental observations in this study. Figure 7 shows the experimental relationship of the furnace maintenance temperature and the freezing plateau duration of the silver cell (from Figure 4), which shows that the freezing plateau duration increases with decreasing furnace temperature differential. According to the analysis, a very long freezing plateau can be obtained if the furnace maintenance temperature is kept very close to the freezing point of the cell. But again, if the furnace temperature happens to drift above the freezing temperature, metal can begin melting instead of freezing and the plateau destroyed. From the authors' experience, it is best to set the furnace maintenance temperature at about 0.4 to 0.5 K below the freezing temperatures for low-temperature fixed-point cells, such as indium, tin, and zinc cells. For high-temperature fixed-point cells, such as aluminum and silver cells, the furnace temperature should be set 0.25 to 0.4 K below the freezing temperatures.

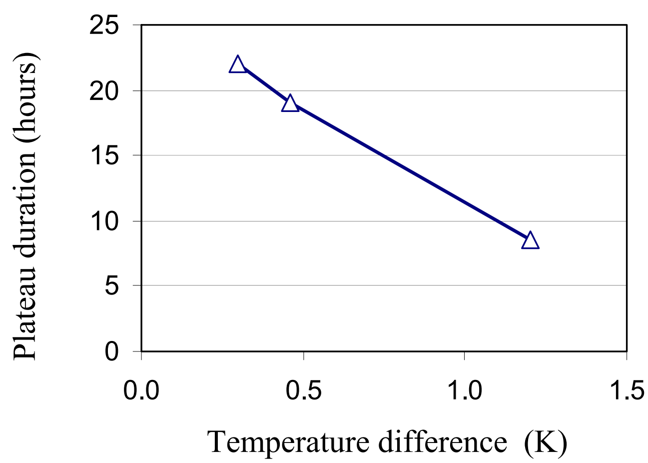

Figure 7. Plateau duration vs. temperature difference for a silver fixed-point cell.

To further analyze the freezing rate in the radial direction, the following equation can be obtained from equation (2):

$$\Delta H \cdot \rho \cdot r \cdot \left(r_0 - r\right) \cdot dr = k \cdot \Delta T \cdot r_0 \cdot dt \tag{5}$$

Reorganization of equation (5) results in the following:

$$r \cdot (r_0 - r) \cdot \frac{dr}{dt} = \frac{k \cdot \Delta T \cdot r_0}{\Delta H \cdot \rho} \qquad (6)$$

It can be seen from equation (6) that the advancement rate of the solid/liquid interface (dr/dt) is proportional to the temperature difference, and it varies continuously during the freezing process as the melt radius *r* changes. To obtain a quantitative relationship between the temperature difference and the advancement rate of the solid/liquid interface, the effective thermal conductivity coefficient *k* can be calculated from the experimental results using equation (4):

$$k = \frac{\Delta H \cdot \rho \cdot \left(r_0^3 - 3r_0 r_1^2 + 2r_1^3\right)}{6r_0 \cdot t \cdot \Delta T} \qquad (7)$$

For the silver cell, taking the value of the latent heat of silver as 105 kJ/kg, the density of silver as 10.5×10^3 kg/m^3, r_0 as 2.5 cm, r_1 as 0.25 cm, ΔT as 0.3 K, and *t* as 22 hours, the calculated effective thermal conductivity coefficient is 4.70 W/(m·K). Using this value in equation (6), the calculated advancement rate of the solid/liquid interface at the beginning of the freeze is 4.8 mm per hour, and the freezing rate becomes 2.0 mm per hour at the end of freezing. The calculated results agree very well with McLaren and Murdock's experimental results. They observed that the advancement rate of the solid/liquid interface is 2 to 5 mm/hour on average during the freezing process [4]. The calculated results also agree well with our experimental observations in this study. Figure 8 gives a comparison of the calculated freezing rate and the observed average freezing rate in the radial direction with a temperature difference of 0.3 K for the silver cell (see Figure 5). The average experimental freezing rate is 1.02 mm/hour ((25-2.5) mm / 22 hour) = 1.02 mm/hour) which is quite close to the calculated results.

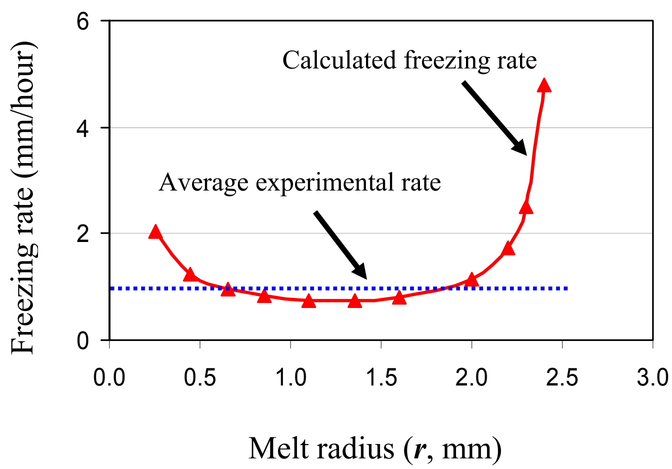

Figure 8. Comparison of the calculated freezing rate (*dr*/*dt*, mm/hour) in the radial direction and the average experimental freezing rate for a silver cell with a temperature difference of 0.3 K.

4. Conclusion

Experiments were carried out in order to investigate the influence of the induction methods, induction time, and furnace maintenance temperature on the quality of the freezing plateau of fixed-point cells. From the experimental results, it is found that insufficient induction can cause overshoot at the beginning of the freezing plateau. According to the experimental results, it is appropriate to set the furnace maintenance temperature about 0.4 to 0.5 K below the freezing temperatures for low-temperature fixed-point cells such as indium, tin, and zinc cells. For high-temperature fixed-point cells such as aluminum and silver cells, the furnace temperature can be set at 0.25 to 0.4 K below the freezing temperatures to produce a long duration freezing plateau.

Theoretical analysis and the experimental observations show that the freezing plateau duration is inversely proportional to the difference of the furnace maintenance temperature and the freezing-point temperature. The advancement rate of the solid/liquid interface in the radial direction increases linearly with the temperature difference, but varies as freezing proceeds because of the changing melt radius.

Acknowledgments

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