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Mechanism to Diminish the Supercooling of the Tin Freezing Point by using Graphite Powder

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Abstract The formation of crystallization centers from extremely pure molten tin is normally associated with deep supercooling. This deep supercooling is inconvenient for the operation of tin freezing-point cells, especially for sealed tin fixed-point cells without a holder to facilitate removal from the furnace. Researchers of the National Institute of Metrology (NIM) intended and succeeded in reducing this deep supercooling by adding fine and pure graphite powders to tin fixed-point cells without influencing the fixed-point temperature, but the mechanism is yet to be properly clarified. The principle of heterogeneous nucleation indicates that a decrease of the contact angle of the crystalline nucleus on the substrate surface results in a significant reduction of supercooling required for initiation of nucleation. The heterogeneous theory is utilized by the authors of this paper to give a reasonable description of the mechanism of supercooling reduction by addition of graphite powder. It is demonstrated that the freezing plateau can be realized by the natural cooling of the tin cell within the furnace without using the 'outside nucleation' technique. The maximum temperature of the freezing curves of the tin cell with graphite powder agrees well with the reference tin cell without the graphite powder, and the cells with graphite powder show good consistency.

Keywords Heterogeneous nucleation · Supercooling · Tin freezing point

1 Introduction

Supercooling appears during the crystallization of pure molten metals. Ovsienko [1] concluded by citing the results of previous studies that the structure of molten

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metals influences the degree of supercooling. Pure metals of loosely packed crystalline structure possess a more complex crystalline structure, the entropy of melting is large, and the transition to the liquid state is characterized by a considerable increase in the interatomic distance. The crystallization of such molten metals requires a significant atomic rearrangement on freezing, leading to a deep supercooling as large as 20–30 K. Tin is a metal of loosely packed crystalline structure [1] that exhibits supercooling of as much as 20–30 K.

The freezing point of pure tin is a fixed point of the International Temperature Scale of 1990 (ITS-90). The deep supercooling of tin leads to the application of the 'outside nucleated' technique [2,3] that makes it inconvenient to realize the tin freezing temperature. The depth of the supercool appears to depend on many variables. McLaren and Murdock [4] surmised that the purity of the tin samples, the addition of a graphite powder topping, and the thermal history of the previous tin melt influence the extent of the supercool. Topping the tin melts with graphite powder was observed by them to decrease significantly the supercooling of extremely pure tin ingots, where graphite powder was applied as an oxide inhibitor. "Inadequate" (<1°C) supercooling was experienced even with extremely pure tin. Because this supercooling was considered inadequate, the graphite-powder topping was omitted thereafter when the samples were loaded. They found that when melts were held <2°C above the liquidus points for <2 h, and then refrozen, the supercooling was usually <4°C. The literature [2] claimed that: "It is important to achieve a high degree of supercooling (>4°C) for the attainment of the plateau temperatures by means of outside nucleated slow freezes. High-purity tin should be kept in an inert atmosphere and not be topped with graphite powder: when graphite powder becomes distributed throughout a sample, inadequate supercooling (<4°C) may result." The literature [2,4] emphasized the importance of adequate supercooling for the realization of freezing curves of tin but did not relate the degree of supercooling to the equilibrium temperature of the tin phase change.

Scientists of National Institute of Metrology (NIM) also observed that a graphite-powder topping decreases the supercooling of freezing tin. Their observations led them to conclude that there is no significant difference in the tin freezing temperature among tin cells with and without a graphite-powder topping. The studies demonstrated that the maximum temperatures of the freezing curves of the tin-sealed cells of fine and pure graphite powder agree with that of the reference tin cell within 0.45 mK. The graphite-powdered cells show adequate uniformity and stability. The mechanism of this supercooling reduction has not been reasonably described before, despite a large number of experimental observations. The authors of this paper intend to give a reasonable description of the mechanism by resorting to the heterogeneous nucleation theory.

2 Mechanism of Supercooling

The process of crystal nucleus formation is either homogeneous or heterogeneous. Homogeneous nucleation deals with the freezing phases that are uniformly and completely formed within the supercooling liquid. According to the homogeneous nucleation theory [1], the temperature-dependent rate of crystallization nucleus formation is

$$J_\mathrm{o} = ZK_\mathrm{o}\mathrm{e}^{-U/(kT)}\mathrm{e}^{-W_\mathrm{o}/(kT)} \tag{1}$$

where J_o is the rate of homogeneous formation of the crystallization centers; Z and K are two coefficients in which K_o is related to the temperature; U denotes the activation energy of an atom transitioning from the liquid phase to the crystal; and W_o is the energy required for the spherical critical nucleus formation, that is,

$$W_\mathrm{o} = \frac{0.6T_\mathrm{o}^3}{N\Delta T^2}\Delta S \tag{2}$$

where ΔS is the entropy change of the phase transition process, from $L = \Delta S T_\mathrm{o}$, where L is the latent heat of melting and T_o is the equilibrium temperature; ΔT denotes the supercooling, $\Delta T = T_\mathrm{o} - T$. The second exponential term of Eq. 1 is the probability for crystallization center formation. For typical metals, the mobility of atoms is very high so the first exponential term $U/(kT)$ of Eq. 1 is small; the rate of crystallization center nucleation is dominated mainly by the probability term. The metastability boundary is abrupt and is characterized by a critical supercooling ΔT_c such that below this critical supercooling $J = 0$, but beyond this critical supercooling, $\Delta T > \Delta T_\mathrm{c}$, J immediately increases to a considerable magnitude. Equation 1 shows that, for homogeneous nucleation, the nucleus formation rate is governed by two factors, the mobility of atoms, i.e., $U/(kT)$, and the energy of critical nucleus formation. For typical metals, the latter term dominates the nucleus formation rate. Equation 1 indicates that homogeneous nucleation is a process without catalyst particles to aid nucleation. For this reason, surprisingly deep supercooling exists with homogeneous nucleus formation.

Generally, deep supercooling with homogeneous nucleation is impossible to achieve in bulk liquid metals because heterogeneous nucleation occurs with much less supercooling on the surface of the container, which is never perfectly polished. A large number of imperfect structures and/or particles are present on the surface of the wall. Those particles and/or structures act as catalysts to decrease the energy required to form a nucleus and thereby increase the rate of nucleation. For heterogeneous nucleation, the energy of nucleus formation at the substrate surface is [1]

$$W_\mathrm{s} = W_\mathrm{o} f(\theta) \tag{3}$$

where W is the energy needed for the crystalline nucleus formation, subscripts s and o denote, respectively, heterogeous and homogeneous nucleation; the term $f(\theta)$ denotes the effect of catalytic activity of the solid substrate surface, where θ is the contact angle

$$f(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4, \quad \cos\theta = \frac{\sigma_\mathrm{sl} - \sigma_\mathrm{sn}}{\sigma_\mathrm{sl}} \tag{4}$$

where σ denotes the surface tension, and the subscripts s, l, and n refer, respectively, to the solid substrate surface, the liquid, and the crystalline nucleus.

$$J_\mathrm{o} = K_\mathrm{s}\mathrm{e}^{-U/(kT)}\mathrm{e}^{-W_\mathrm{s}/kT)} \tag{5}$$

The difference between homogeneous and heterogeneous nucleation exists due to the catalytic activity of the solid substrate surface. A substrate surface without catalytic activity for liquids is completely nonwettable, $\theta = 180°\text{C}$ and $W_s = W_o$. Liquids on this kind of substrate surface form a perfectly spherical drop (or would do so, if not for the influence of gravity) and the nucleation is homogeneous without the effect of catalytic activity by the wall surface. In the case of perfect wetting, $\theta = 0°\text{C}$, $f(\theta) = 0$, and $W_s = 0$; the nucleation occurs at zero supercooling. Normally, $0°\text{C} < \theta < 180°\text{C}$ and the nucleation is heterogeneous.

3 Procedure for Diminishing Supercooling

The Supplementary Information for the International Temperature Scale of 1990 [2] recommends that tin fixed-point devices be fabricated by holding a tin ingot in a cylindrical graphite crucible of extremely high purity, and the crucible assembly is then held in a cylindrical Pyrex or fused silica holder. Obviously, the heat released by the freezing tin ingot will be mainly transferred through the wall of the crucible. The substrate surface touching the tin melt has the lowest temperature. Nucleus formation must be heterogeneous for the freeze of any tin melt in a fixed-point cell.

Since the mid-1990s, scientists at NIM have applied traces of extremely fine and pure graphite powder to the wall of the graphite crucible when fabricating sealed tin cells (Y.N. Wang, co-author of this paper, initiated this technique). The graphite powders have diameters on the scale of micrometers and have the same purity as the bulk graphite of the crucible. The fine powders are found to distribute spontaneously on the wall of the crucible because of the molecular adhesion force [3]. This distribution yields a thin porous layer of fine graphite powder. Referring to the literature [5], the surface tension generates the capillary effect when liquids wet the porous layer which promotes the affinity and wettability between the liquid and the porous layer substrate surface. This affinity interaction between fine graphite particles and liquids strengthens the catalytic activity of the surface of the graphite crucible. According to Eq. 4, the increasing affinity and wettability of liquids on the substrate surely decrease the energy and supercooling associated with nucleus formation.

One tin cell, operated for the past 10 years, was recently broken. Fine graphite powder was observed adhering to the wall surface of the graphite crucible to form a porous substrate. The supercooling in the cells treated with this technique is observed to decrease to 2–5 K depending on the thermal history of the molten tin, as indicated in the literature [4]; the lower the temperature of the molten tin, the smaller the supercooling. The small supercooling makes possible a natural cooling operation, whereby a tin fixed-point cell is cooled down naturally within a furnace to realize the tin freezing point. Before cooling, the furnace temperature is set 10°C below the tin freezing temperature.

4 Measurement

NIM has used tin ingots of 6 N purity to fabricate tin cells. The melting and freezing curves of a graphite-powdered cell of tin were measured recently. The furnace is

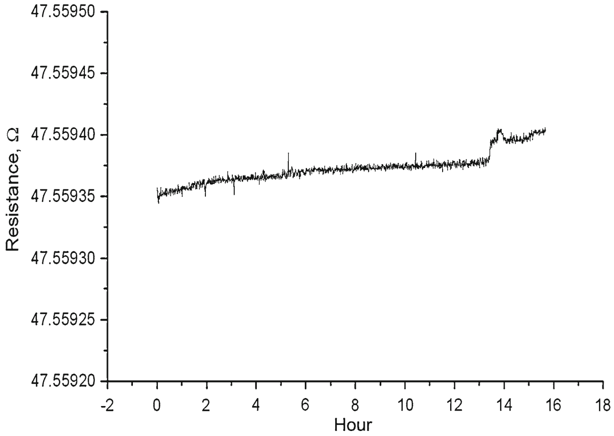

Fig. 1 Melting plateau of the sealed graphite-powdered cell of tin

constructed at NIM and is a three-zone type controlled by one main programmable controller (Shimaden FP23) and two slave controllers (SR23). The furnace temperature is measured by three industrial platinum resistance thermometers with an annual stability better than 0.05°C. Figure 1 illustrates one melting curve of the graphite-powdered tin cell. The temperature of the cell was monitored by a 25-Ω standard platinum resistance thermometer (SPRT). An ASL F18 bridge was used to read the resistance of the SPRT. Before melting, the cell was thermally annealed overnight at a temperature about 1°C below the liquidus temperature. Then, the cell was heated slowly over an hour to the tin melting temperature. Two steel rods were pre-heated in an annealing furnace to 400°C to induce an inner liquid–solid interface in the cell. Once the SPRT indicated the temperature of the cell was within 2 mK of the liquidus temperature, the inner liquid–solid interface was induced by inserting the two pre-heated steel rods into the thermometer entrance well of the cell in sequence. Each hot rod stayed in the cell for 1 min. The temperature of the furnace was set to 1°C above the melting point. The melting plateau remains within a temperature variation of 0.3 mK for up to 13.5 h.

Before realizing the freezing curves of the graphite-powdered cell, the furnace temperature was maintained 1°C above the liquidus temperature to keep the tin in the molten state overnight. When realizing freezing curves, the main temperature controller of the furnace was set 10°C below the liquidus temperature as the first step. The cell then cooled naturally within the furnace. The freezing recalescence was observed to occur within 3.0°C below the liquidus temperature of tin. Once the SPRT indicated the recalescence, two steel rods at room temperature were inserted into the cell in sequence to induce the inner solid-liquid interface. The main controller was then set to heat the furnace to1°C below the liquidus temperature within 40 min. Figure 2 illustrates one freezing curve. The freezing plateau remains within a temperature variation of 0.4 mK for up to 18.7 h. The uncertainty budget to realize the freezing curves with the graphite-powdered cell is listed in Table 1.

The freezing temperature of this graphite-powdered cell was compared 10 years ago in NIM [6] with that of the open tin cell participating in the CCT-K3 comparison.

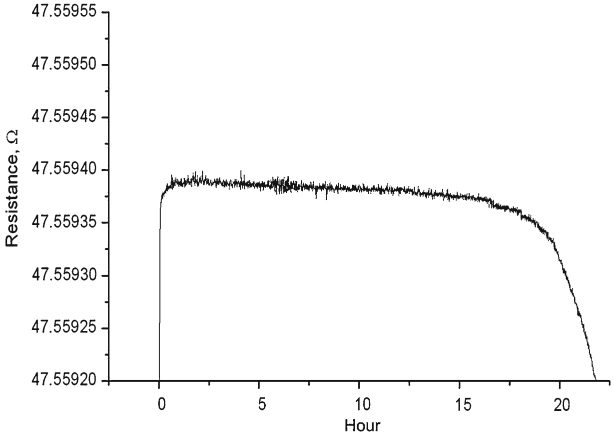

Fig. 2 Freezing plateau of the sealed graphite-powdered cell of tin

Table 1 Uncertainty budget for realizing the freezing and melting curves of tin

Source of uncertainty	Type	Uncertainty of component (mK)
Repeatability of resistance reading	A	0.03
Reproducibility of thermal state	A	0.15
Impurities	B	0.25
Hydrostatic pressure correction	B	0.19
Immersion	B	0.03
SPRT self-heating correction	B	0.03
Propagated from the triple point of water	B	0.10
Bridge stability	B	0.01
Bridge non-linearity	B	0.01
Bridge accuracy	B	0.05
Total standard uncertainty		0.37
Expanded uncertainty ($k = 2$)		0.74

That open cell was made without applying fine graphite powder. The comparison was made by alternately measuring the freezing temperature of both cells with a SPRT. A Guildline Model 9975 bridge was used to measure the resistance ratio of the SPRT with respect to a standard resistor. This SPRT had a stability better than 0.1 mK at the triple point of water before and after the comparison. The maximum temperature of the tin freezing curve of the sealed cell is 0.45 mK above that of the open cell. The final report of the CCT-K3 comparison [7] indicated that the freezing point of the open cell is 1.3 mK lower than the CCT-K3 reference value. The literature [4,8,9] indicated that the impurities with an equilibrium distribution coefficient $k < 1$ depress the freezing point. This open cell was fabricated in the 1970s. The freezing behavior of this cell demonstrated that it was very likely to be contaminated by impurities. The comparison demonstrated that the freezing temperature of the graphite-powdered cell was closer to the reference value of the K3 comparison. The graphite-powdered cell was made in the mid-1990s, and the tin ingot in the cell was less contaminated by impurities than the open cell. The uncertainty budget of this comparison is in Table 2.

Table 2 Uncertainty budget for the comparison of cells

Source of uncertainty	Type	Uncertainty of component (mK)
Repeatability of resistance reading	A	0.03
Stability of SPRT	B	0.10
Bridge stability	B	0.10
Bridge non-linearity	B	0.01
Bridge accuracy	B	0.10
Total standard uncertainty		0.18
Expanded uncertainty ($k = 2$)		0.36

Table 3 Comparison of different sealed cells

Cell No.	1	2	3
Freezing W_{sn}	1.8923869	1.8923866	1.8923855
$\mathrm{d}T_{\max}$ (mK)		0.38	

The freezing temperatures of different graphite-powdered cells of tin were compared following the same procedure as the above comparison. The results are listed in Table 3. The maximum temperature difference among the three different graphite-powdered cells is 0.38 mK, indicating good consistency among those cells.

5 Conclusion

The formation rate of homogeneous and heterogeneous nucleation is dominated by the probability of nucleus crystallization center formation. For homogeneous nucleation, an extremely deep supercooling is needed to initiate crystallization. However, for heterogeneous nucleation, the effect of catalytic activity of the solid substrate surface makes the energy (or the supercooling) required for nucleus formation decrease significantly. The stronger the catalytic activity of the substrate surface, the lower the supercooling that is required. Nevertheless, the homogeneous and heterogeneous nucleation mechanisms show that the equilibrium temperature is not related to the supercooling required to initiate crystallization. Therefore, the decrease of the supercooling enhances heterogeneous nucleation without influencing the equilibrium temperature of the phase change. The application of the fine and pure graphite powder promotes the wettability and the catalytic activity at the surface of the graphite crucible to significantly decrease the required supercooling . Because the purity of the graphite powder is the same as the bulk graphite of the crucible, it is reasonable to believe that the application of the fine and pure graphite powder does not introduce additional contamination to the graphite-powdered cells and has no influence on the equilibrium temperature of freezing tin.

Scientists of NIM have applied fine and pure graphite powder to the walls of graphite crucibles when fabricating tin cells. The supercooling of those graphite-powdered cells has been observed to decrease significantly to 2–5 K. With this treatment technique, the freezing of the graphite-powdered cells can be simply obtained by natural cooling instead of the "outside nucleated slow freeze" operation. The freezing and melting curves realized by this natural cooling procedure are quite flat. The freezing plateau remained within a temperature variation of 0.4 mK for up to 18.7 h, and the melting plateau remained within a temperature variation of 0.3 mK for up to 13.5 h. The comparison shows that the maximum freezing temperature of a graphite-powdered cell is 0.45 mK above that of the national standard. This higher indication is closer to the reference value of the K3 comparison. The inconsistency of the three graphite-powdered cells was measured to be 0.38 mK at their maximum difference.

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