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The Influence of Antimony on the Tin Point

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Abstract In 2005, an agreement was reached on how to estimate uncertainties and how to correct fixed-point temperatures for the influence of chemical impurities. Although the general procedure is now specified, some problems remain. The slope of the liquidus line at very low-impurity concentrations must be extracted either from binary-phase diagrams or from doping experiments. Apart from this, there is little experimental evidence to prove that the models used to characterize the freezing and the melting plateaux are adequate, especially for impurities that increase the fixed-point temperature. Therefore, a series of measurements were carried out using a tin fixed-point cell doped with antimony. By varying the freezing and the melting conditions, some useful experimental data were collected.

Keywords Antimony doping · ITS-90 · Tin freezing point · Tin melting point

1 Introduction

The influence of impurities on the fixed-point temperature is one of the major components of the uncertainty budget of fixed-point measurements. Since 2005 thermometrists have agreed on the methodologies for the estimation of uncertainties and correction of fixed-point temperatures attributable to this influence [1]. Several former investigations have been carried out in order to evaluate the effects of impurities on the freezing and melting curves of tin [2–6]. The majority of impurities decrease the freezing temperature of tin. Exceptions are impurities with greater solubility in the solid

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than in the liquid phase, the best known example being antimony, which elevates the freezing temperature of tin. Although the tin–antimony binary-phase diagram and the slope of the liquidus line were investigated down to a concentration of $1\,\mu g \cdot g^{-1}$[2], some questions remain concerning the uncertainty of the slope of the liquidus line and its dependence on residual impurities. Can specific impurities be detected by varying the fixed-point realization procedures, for example, by observing freezing and melting curves with or without an induced second interface surrounding the thermometer well or by realizing melting curves following fast and slow freezes?

A series of experiments were carried out using a tin fixed-point cell after successively doping it with antimony.

2 Experimental Facility

For these investigations, an open fixed-point cell containing about 750 g of tin was used in an argon atmosphere. The length of the graphite crucible was 237 mm, and its outer and inner diameters were 43.5 mm and 35 mm, respectively. The graphite re-entrant thermometer well was 222-mm long, and it had an outer and an inner diameter of 15.5 mm and 10.5 mm, respectively. The crucible was contained in a closed-end-quartz tube of about 50 mm in diameter and 500 mm in length. The quartz tube had a stainless steel lid with an o-ring seal to allow evacuation of the cell and filling with argon. The tin ingot had been used for many years in a tin fixed-point cell and gradually became contaminated. This contaminated tin was used to investigate by how much the melting and freezing ranges would decrease. Then, the results were compared with that of [2], and the slope of the liquidus line was investigated for reproducibility using a system of different purity. The initial freezing temperature of this cell was 2.7 mK below that of the national standard tin fixed-point cell of PTB. Furthermore, the freezing and melting curves of this cell had considerable slope, indicating the existence of liquid-soluble impurities.

The thermometer used for the investigation was a standard platinum-resistance thermometer (SPRT) no. 1054 produced by the Yellow Springs Instrument Company. During the experiments, the resistance of the SPRT was regularly determined at the triple point of water (TPW) in order to test its stability. Table 1 shows the results of those measurements. The maximum temperature difference was found to be 0.12 mK during these measurements. The resistance of the SPRT was measured using a Measurement International Model 6010-T bridge. A Model 9114 furnace, manufactured by

Table 1 Stability inspection of the SPRT by measuring the triple point of water

Date	R (Ω)	Standard deviation $\sigma \times 10^6$ (Ω)
10-10-2006	25.5481030	12
20-10-2006	25.5481149	2.7
20-11-2006	25.5481070	2.8
08-01-2007	25.5481068	2.3
06-02-2007	25.5481174	1.8

Note: R denotes the resistance of the SPRT

Fluke/Hart Scientific, was used in these experiments. To realize the freezing and melting curves, the furnace temperature was set 1.2 K lower and higher than the freezing-point temperature of tin, respectively. Because tin is known to exhibit considerable supercooling, the fixed-point cell was removed for several minutes from the furnace to initiate nucleation.

3 Results and Discussion

3.1 Doping Experiments

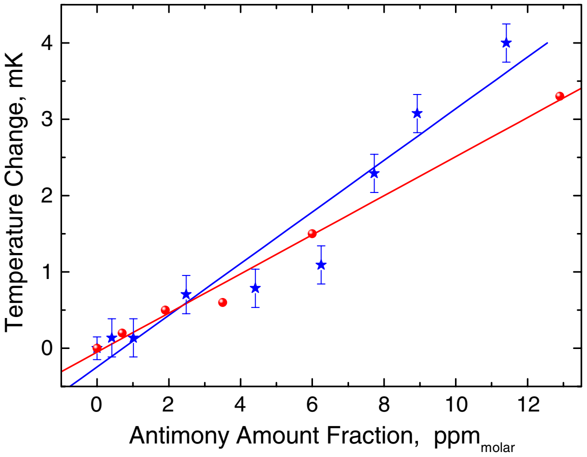
After filling a new graphite crucible with the tin ingot, several freezing and melting plateaux were realized in order to characterize the initial state of the fixed-point cell and the repeatability of the fixed-point realization. The repeatability of the fixed-point realization (maximum of the freezing curve) was found to be within ±0.25 mK, based on, at least, three freezing-curve realizations. Subsequently, the cell was doped with antimony eight times, and several freezing and melting plateaux were realized after each doping. The mass of antimony used for the doping was determined by means of a Sartorius microbalance, Model Micro M500P. The uncertainty of the mass determination was less than 10 μg, equivalent to a temperature uncertainty of about 25 μK.

We noticed that the magnitude of supercooling decreased with increasing antimony concentration. Consequently, after the third doping (corresponding to an antimony fraction of about 2.5 ppm), it was no longer necessary to remove the fixed-point cell from the furnace to initiate freezing (outside nucleation). The furnace temperature setting of 1.2 K below the freezing temperature was sufficiently low for nucleation to occur spontaneously. Due to the much larger heat loss during outside nucleation, freezing plateaux of the outside-nucleated ingot are shorter than the ones nucleated in the furnace. For our experimental conditions, the difference was found to be about one-third of the freezing time. Nevertheless, the maximum of the freezing curves was found to be insensitive to different initiation procedures.

As expected [2], the freezing-point temperatures, as determined from the maxima of the freezing curves, increase with increasing antimony content. Figure 1 shows the maximum temperatures of the freezing curves as a function of antimony concentration. At low concentrations, one would expect a linear relationship between the amount of impurity and the freezing temperature. Our results yield a slope for the liquidus line of $0.34\,\mathrm{mK}\cdot(\mathrm{ppm\ atomic})^{-1}$. Connolly and McAllan obtained a value of $0.26\,\mathrm{mK}\cdot(\mathrm{ppm\ atomic})^{-1}$ [2], see Fig. 1 (For this calculation, only the results of [2] for concentrations <12 ppm were used.)

Our results deviate from the expected linear curve and these deviations exceed the typical repeatability of the fixed-point realizations and the uncertainties of the mass determinations. The repeatability of the maximum of the freezing curve (indicated by the error bars in Fig. 1) was derived from at least three consecutive fixed-point realizations. In order to find an explanation for the unexpected behavior, a second series of six measurements was carried out with the highest impurity concentration (11.3 ppm) about two months later. A new fixed-point temperature was determined

Fig. 1 Variation of the maximum temperature of freezing curves with the antimony amount fraction (blue stars—results of the present work, red dots—results from Connolly et al. [2])



which was about 0.6 mK below the mean of the first series. To assure a sufficiently low influence of the cell pressure, the cell was evacuated and filled with argon before each measurement series. At the beginning of the first melting or freezing plateau, the pressure was adjusted. It was found that a variation of the maximum temperature of freezing curves of up to 1 mk is possible, depending on how the impurities are distributed in the liquid phase at the beginning of the freeze. This behavior was especially pronounced after a long freeze (about 20-h duration) followed by melting with a furnace temperature of 1 K above the fixed-point temperature. Although the tin was in the liquid state for several hours, the subsequent freezing plateau resulted in a low fixed-point temperature. In contrast, melting with a furnace setpoint about 15 K above the liquidus temperature and keeping the tin at this temperature overnight resulted in considerably higher and more repeatable fixed-point temperatures. We attribute this behavior to the segregation of impurities during slow freezing and incomplete mixing in the liquid state. Therefore, we consider the observed nonlinear liquidus slope an apparent one caused by an inhomogeneous impurity distribution.

3.2 Segregation Experiments

We also investigated the influence of freezing on the subsequent melting plateaux. Different freezing procedures yield different impurity distributions in the solid ingot. Figure 2 shows the melting plateaux of the cell doped with 2.5 ppm antimony after fast and slow freezing (about 10 min and about 15 h, respectively). The melting curves following fast freezing had a considerably steeper approach to the melting temperature and much smaller melting slopes than those of slowly frozen ones. In order to see if crystal defects influence the melting plateau, the ingot was annealed at 230.7 °C for more than 48 h after fast freezing. However, no difference was found between the melting curves of the annealed and the un-annealed ingots. The observed behavior is therefore attributed to different distributions of impurities after fast and slow freezing.

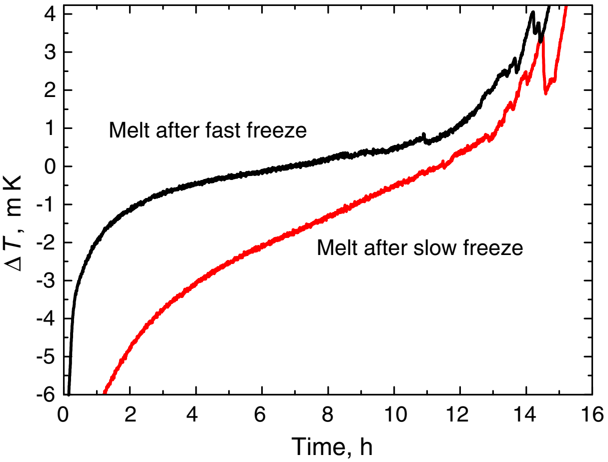


Fig. 2 Melting curves after fast and slow freezing without an inner interface at an antimony amount fraction of 2.5 ppm

In the next melting experiment, a liquid interface was created along the thermometer well by inserting a quartz rod that was pre-heated in a second furnace to 350 °C. During melting, as mentioned earlier, the furnace temperature was about 1.2 K above the liquidus point. When the measured temperature was less than 10 mK below the liquidus temperature, the SPRT was removed and transferred into the pre heating well of the furnace while the pre-heated quartz rod was inserted into the fixed-point cell for one minute. On re-transfer of the SPRT into the fixed-point cell, the temperature of the thermometer dropped by about 2 K. This procedure was repeated twice. Figure 3 shows the melting curves after fast and slow-freezes for the ingot containing 8.9 ppm antimony. The liquid interface along the thermometer well did not change the difference between the melting curves. Due to the overheated liquid layer generated along the well after inserting the hot quartz rod, a peak was detected. During each slow-freezing experiment (in contrast to fast freezing), a solid interface was induced along the thermometer well in order to obtain accurate freezing plateaux. It was assumed that, during inducement of the solid layer along the well (during a freezing measurement), a considerable amount of antimony accumulated around the thermometer well. Thus, subsequent re-melting of the antimony-rich region around the thermometer well should result in a higher initial melting temperature. In order to see if this is indeed what happens, slow-freezing plateaux were realized without initiating an inner interface around the thermometer well using the 11.4 ppm sample. The melting curve with an induced inner interface along the well shows a much smaller peak (see Fig. 4), as expected. It seems, then, that in this way one can test whether a fixed-point cell contains impurities with higher solubility in the solid than in the liquid phase.

4 Conclusions

The influence of antimony on melting and freezing temperatures of tin was measured between 0.41 ppm atomic and 11.4 ppm atomic concentrations. Measurements were

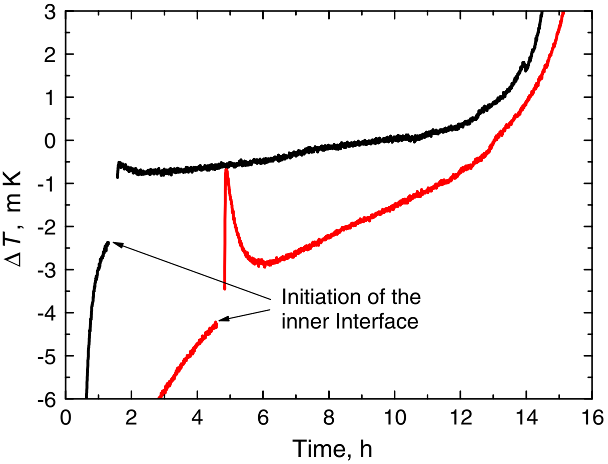


Fig. 3 Melting curves after fast and slow freezing with inner interface at an antimony amount fraction of 8.9 ppm

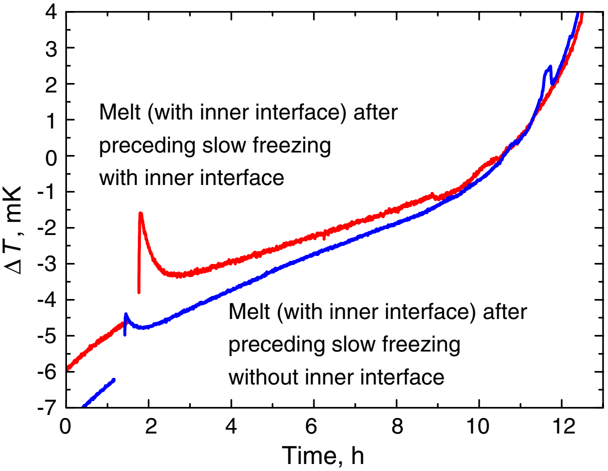


Fig. 4 Melting curves with inner interface after slow freezing with and without inner interface (antimony amount fraction of 11.4 ppm)

carried out under different experimental conditions with the following main results. First, the temperatures of both the freezing and melting curves increased with increasing antimony concentration, in reasonable agreement with previous investigations [2]. Second, with increasing antimony concentration, the depth of supercooling was considerably reduced. Third, melting curves following fast freezes had plateaux of much smaller slope than those following slow freezes. This is most likely due to different impurity distributions (segregation) within the solid ingots. Fourth, annealing following fast freezing had no effect. Therefore, the difference between the melting curves after fast and slow freezing is attributed to different impurity distributions. Fifth, melting curves with a second interface along the thermometer well exhibit a peak due to overheated liquid around the re-entrant well and, partly, from accumulated antimony. The size of the peak depends on the previous freezing conditions. By comparing the height and width of this peak following different nucleation methods during previous freezing, one can find out if a fixed-point cell contains impurities which have greater solubility in the solid than in the liquid phase.

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