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A New Method for the Quantification and Correction of Thermal Effects on the Realization of Fixed Points

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Abstract The temperature and flatness (shape) of a fixed-point plateau depend on both the amount and nature of specific impurities and on thermal effects that are influenced by the fixed-point cell design and furnace properties. A better understanding and experimental proof of the influence of specific impurities on fixed-point realizations require the separation of impurity influences from thermal effects. In this paper the influence of heat exchange between the thermometer and furnace is quantified via a method based on changing the furnace temperature during the fixed-point measurement. It will be shown that the corresponding correction of this thermal effect has a dominant influence on the plateau shape compared to the influence of impurities. This leads to an explanation for why the maximum of an induced freeze is the most reproducible temperature. A secondary outcome is an explanation of why natural freezes have less flat plateaux compared to induced freezes, resulting in fixed-point temperatures that are too low. Furthermore, the suggested procedure is the basis of the direct and quantitative comparison of fixed-point cells and the detection of weak points within a specific design. It allows optimization of fixed-point cells and furnaces, and helps to deepen the common understanding of the phase transition in fixed-point cells.

Keywords Heat conduction · Induced freeze · ITS-90 · Temperature fixed points · Thermal correction · Uncertainty budget · Natural freeze

1 Introduction

The fixed-point temperature of most metallic fixed points of the ITS-90 is realized according to [1,2] as the maximum of the measured temperature in the freezing

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fixed-point cell. Usually, deviations from that temperature, i.e., the shape of the temperature plateau, are attributed to the response function of the thermometer and to the impurities in the fixed-point material. To describe the latter influences, different models are used [3–7].

For recently made fixed-point cells at PTB, chemical analyses of the materials indicate a total amount of impurities of less than 1 ppm or even 100 ppb, which is in agreement with typical fixed-point temperature deviations (in terms of the maximum of the plateau for an induced freeze) of less than 0.5 mK. Nevertheless, considerable inconsistencies have been found when the characteristics of the plateaux were compared with the expected behavior according to the previously mentioned models.

Discrepancies were found if the shape of freezing curves following the maximum temperature was analyzed, even if the impurity content was overestimated and very different behavior (e.g., complete equilibrium mixing in the liquid state or no mixing) was assumed.

As a second example, the initial part of a natural freezing curve may have a duration of several hours, which may be extended to as long as a few days (by setting the furnace temperature close enough to the fixed-point temperature) before the maximum is achieved. Neither the response function of the thermometer nor the heat capacity of the fixed-point cell (including the metal) can be the reason because, for example, the new steady-state temperature is indicated less than 5 min after changing the pressure of the fixed-point cell.

The key to understanding these oddities is the failure to account for heat conduction between the sensing element of the thermometer, the environment, and the furnace. To investigate this effect, the temperature of the furnace is changed in a stepwise manner during the fixed-point's phase transition and the resulting impact on the measured temperature observed, as suggested in [1,8]. In this context, we introduce a quantity (ratio) μ_{furnace} that specifies how much the measured fixed-point temperature changes when the furnace temperature is changed. At the beginning of most phase transitions, when there is a perfect phase boundary, the measurement of μ_{furnace} yields very small values. Depending on how well the furnace-temperature profile characteristics fit the needs of the fixed-point cell, at the end of the phase transition there will eventually be thermal bridges, i.e., completely molten or frozen regions in the cell, whose detection and dominating influence on the plateau shape will be demonstrated here. Consequently, we propose to correct the recorded shape of the phase transition for thermal influences, and to optimize the furnace and the fixed-point cell to reduce the impact of this effect.

Beyond that, we investigate the influence of a second (inner) phase boundary, compare results from two zinc fixed-point cells with different designs, and show the variation in the influence of heat conduction at different heights within a fixed-point cell, also suggesting a correction to immersion profiles.

2 Fundamentals

An ideal fixed-point measurement should be made under adiabatic conditions so that the temperatures of the thermometer T_{meas}, the phase interface T_{fp}, the furnace T_{furnace}, and the environment T_{ext} are identical. For a practical measurement, the thermometer should be surrounded by a solid–liquid interface as far as possible, to avoid thermal links to zones with a different temperature. In order to estimate their influence on the measured temperature, we distinguish between two contributions: first, the heat exchange between the thermometer and the isothermal part of the furnace surrounding the fixed-point cell and, second, the heat exchange between (the sensing part of) the thermometer and the external surroundings (including the upper parts of the furnace). Thus,

$$T_{\mathrm{meas}} = T_{\mathrm{fp}} + \mu_{\mathrm{furnace}}(T_{\mathrm{furnace}} - T_{\mathrm{fp}}) + \mu_{\mathrm{ext}}(T_{\mathrm{ext}} - T_{\mathrm{fp}}) \tag{1}$$

where the parameters μ_i (we refer to them as penetration ratios) are not constants, but are different for every fixed-point cell design, material, furnace (temperature profile), and they even change with time when a phase transition takes place because the shape of the phase boundary changes and, hence, the thermal contact to the thermometer changes as well. Nevertheless, the $\mu_i(t)$ are reproducible and can be measured for a specific fixed-point realization. Instead of complete modeling of a fixed-point cell and its environment, which is beyond the scope of this document, we will demonstrate how these μ_i can be experimentally determined. According to Eq. 1, if the temperature of one heat source is changed by ΔT_i, without affecting the temperature of all other heat sources and without any change to the experimental setup itself, the resulting temperature T_{meas} will change like

$$\Delta T_{\mathrm{meas}} = \mu_i \Delta T_i \tag{2}$$

The best available fixed-point realization would yield $\mu_i = 0$ (no influence); the worst case is $\mu_i = 1$.

This model assumes a stable and homogeneous temperature of the phase boundary, which is not necessarily true. While temperature inhomogeneities at the phase boundary (e.g., due to the hydrostatic-head effect) do not affect the validity of Eq. 2, influences of impurities and diffusion cannot be treated properly. Different melting and freezing rates induce different impurity distributions in the region near the phase boundary due to slow diffusion [9] in the liquid phase, which causes temperatures at the phase boundary to depend on the interfacial velocity [10]. In terms of the equations above, in particular, Eq. 2, T_{fp} will slightly change and thus T_{meas} will too. This is more obvious if Eq. 1 is rewritten to show T_{meas} as a weighted mean dependent on the various coupling factors:

$$T_{\mathrm{meas}} = (1 - \mu_{\mathrm{furnace}} - \mu_{\mathrm{ext}})T_{\mathrm{fp}} + \mu_{\mathrm{furnace}} T_{\mathrm{furnace}} + \mu_{\mathrm{ext}} T_{\mathrm{ext}} \tag{3}$$

Hence, when the furnace temperature is changed, the resulting change of the measured temperature consists of two parts: the impurity-related effects (included in T_{fp}) and the thermal effects. The presumption of the following work is that the influence of the diffusion-related effects can be neglected in favor of the dominant influences of heat conduction. Although we cannot prove this directly, there is convincing evidence that will be presented here.

This paper is focused on estimating the influence of heat conduction between the furnace and the thermometer. The influence of room temperature, i.e., μ_{ext}, is not addressed here.

3 Setup and Data Evaluation

The zinc fixed-points cells that we used were manufactured at PTB following a common design and filled with commercially available fixed-point material of nominal 6 N purity. The resistance of the thermometer (Model 5681 from Hart Scientific) was measured by an Automatic Systems Laboratories Model F900 AC resistance ratio bridge. A Fluke/Hart Scientific Model 9114 three-zone furnace was used. A measure of the homogeneity of the furnace temperature was derived from the immersion characteristics (15 cm) of the SPRT in the fixed-point cell with the ingot in the solid state and at a temperature a few kelvin below its liquidus temperature. The resulting temperature variations were smaller than 100 mK. The furnace temperatures were changed via an external computer every 40 min in a sequence like: $T_{\text{fp}} - 1\,\text{K}$, $T_{\text{fp}} - 0.5\,\text{K}$, T_{fp}, $T_{\text{fp}} - 0.5\,\text{K}$, $T_{\text{fp}} - 1\,\text{K}$, etc. In this case, it takes the furnace itself only a few minutes to stabilize at each temperature, whereas the whole system including the fixed-point cell and thermometer need up to 10 min, because of the heat capacity of the fixed-point assembly.

Figure 1 shows an example of a programmed sequence of the furnace temperature and the resulting temperature measured in a zinc fixed-point cell. For a reliable estimation of μ_{furnace} by means of Eq. 2, (at least) two temperature values are needed, related to two different furnace temperatures for exactly the same state of the fixed-point cell. Thus, the temperature curves have to be extrapolated to the points where the temperature of the furnace changes. The procedure is illustrated in Fig. 2 in more detail. The encircled points in both figures are the extrapolated temperature values whose differences are used to calculate the furnace-related penetration ratio (applying to fixed-point cell and furnace) μ_{furnace} according to Eq. 2.

The uncertainties of the temperature differences obtained are estimated to be at least 50 μK. Furthermore, they increase with increasing changes of T_{furnace} due to the uncertainty of the extrapolation. This is partly due to the heat capacity of the fixed-point cell and partly due to influences of the furnace-temperature instability that become greater with increasing μ_{furnace}.

Evidently, the μ_i must not change when the furnace temperature is changed in order to make an estimate possible. As a consequence, when a freeze is being investigated, the temperature may not be set higher than the fixed-point temperature. Otherwise, parts of the cell will re-melt, new phase boundaries will occur, and hence the thermal resistances and all μ_i's will change. Likewise, the furnace temperature must not be set below the fixed-point temperature for a melt. Furthermore, special attention must be paid to the homogeneity of the temperature distribution in the furnace to avoid parts of the cell becoming too cold or too warm. This is checked by an immersion measurement using a cell filled with alumina powder.

Figure 3 shows the equivalence of measurements obtained with periodically adjusted furnace temperatures and common freezing plateaux. As the freezing

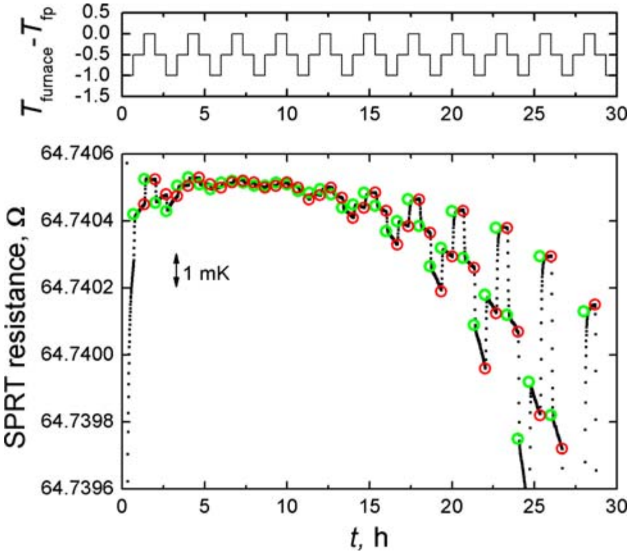

Fig. 1 Adjusted furnace temperature (relative to the fixed-point temperature) and measured SPRT resistance as a function of time for non-induced freezing of a zinc fixed-point cell. Encircled points are taken for evaluation purposes

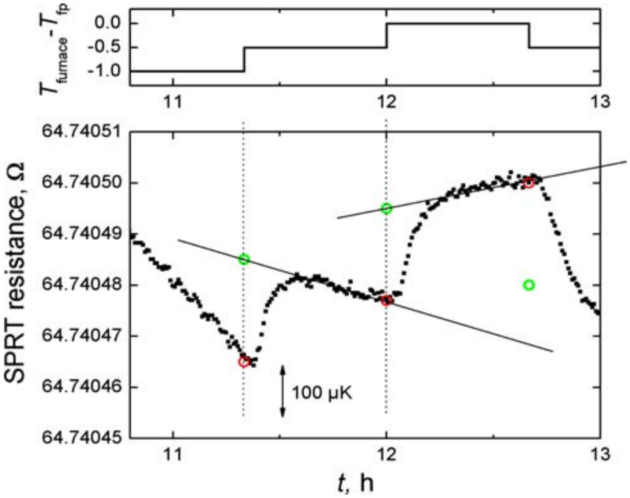

Fig. 2 Illustration of the extrapolation procedure applied to the data of Fig. 1

plateaux for different static furnace temperatures are of different duration, they have to be rescaled to a quantity such as the molten fraction of metal, F, in order to be compared. In doing so, the shape of the plateau with a switching furnace temperature alters because F will be a nonlinear function of time (F decreases faster for a furnace temperature of $T_{\text{fp}} - 1\,\text{K}$ than for T_{fp}). That is why the same measurement, the black curve, looks different as in Fig. 1.

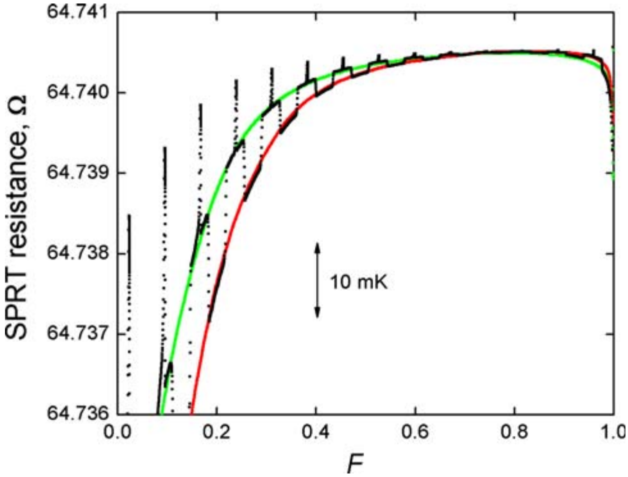

Fig. 3 Same zinc-cell freezing plateau as in Fig. 1 (non-induced freeze, furnace temperature periodically switched among T_{fp}, $T_{\mathrm{fp}} - 0.5\,\mathrm{K}$, and $T_{\mathrm{fp}} - 1.0\,\mathrm{K}$) as a function of the molten metal fraction (black dots) in comparison with conventional zinc freezing plateaux with furnace temperatures fixed at 0.5 K (green line) and 1.0 K (red line) below the fixed-point temperature, respectively. Note: Time increases from right to left

The red and green curves in Fig. 3 show induced freezes, the former with $T_{\mathrm{furnace}} = T_{\mathrm{fp}} - 1\,\mathrm{K}$ and the latter for $T_{\mathrm{furnace}} = T_{\mathrm{fp}} - 0.5\,\mathrm{K}$. For the measurements with a second solid–liquid interface, a cold (room temperature) quartz rod was inserted into the thermometer well for one minute while the SPRT was kept in the preheating well of the furnace. Contrary to the common belief that these curves treated as a function of F should be almost identical, they show considerable differences, e.g., of several tens of mK in the first 70% of the plateau, which can be explained by influences of heat conduction. Obviously, the black curve (with a switched furnace temperature) shows how the fixed-point temperature can be switched between the standard fixed-point plateaux. Taking into account that $F = 0$ and $F = 1$ can be estimated with an uncertainty of only several percent, there is good agreement among the three curves.

4 Initiation-Related Effects

A detailed comparison of the plateaux of the four possible fixed-point realizations (freeze and melt, each with and without a second (inner) phase boundary) reveals a substantial asymmetry given that that three of them achieve a temperature very close to the fixed-point temperature after a short time and a very flat plateau while the fourth, the non-induced freeze, does not. In other words, initiation improves the fixed-point realization considerably if it is a freeze, while for melts, the changes due to a second (inner) interface are much smaller. It seems clear that an explanation must be based on the phenomenon of supercooling since an analogous "overheating" during the melting of fixed-point material does not occur.

The measurement shown in Fig. 1 suggests an explanation that relies on a considerable influence of heat exchange between the thermometer and furnace. As is shown,

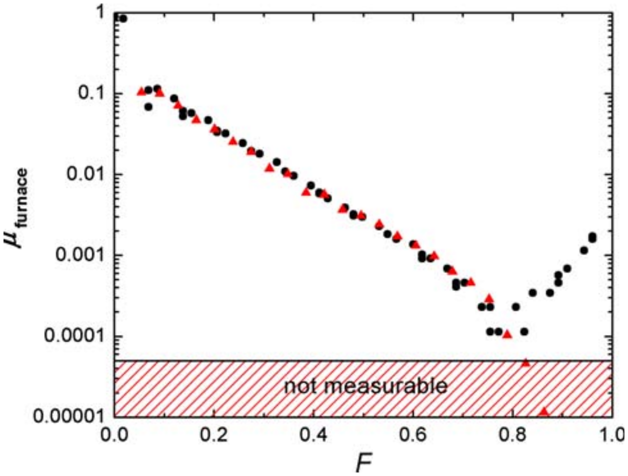

Fig. 4 Penetration ratio μ_{furnace}, i.e., the influence of heat conduction to the furnace, as a function of molten fraction of material during a freeze of a zinc fixed-point cell: ▲—induced freeze, furnace set to $T_{\text{fp}} - 0.5$ K and $T_{\text{fp}} - 1.5$ K; •—non-induced freeze, furnace set to T_{fp}, $T_{\text{fp}} - 0.5$ K, and $T_{\text{fp}} - 1.0$ K

the measured temperature of the cell is very close to the fixed-point temperature when the furnace temperature is set to a value near the fixed-point temperature, while the temperature drops more than 1 mK when the furnace temperature is set 1 K lower. In other words, there is a distinct influence of the furnace temperature on the measured temperature in the fixed-point cell, not only at the end of the freeze but also at the beginning. As T_{meas} is apparently very close to T_{fp} when the T_{furnace} is set to T_{fp}, heat conduction to the furnace must be the dominant influence. Thus, an understanding of the slow approximation of the fixed-point temperature for a non-induced freeze in the first 20% of the plateau as a time-related effect must be incorrect. Indeed, the temperature in the diagram jumps relatively fast as a result of a change in the furnace temperature.

Figure 4 shows the calculated μ_{furnace} as a function of F for the same data (non-induced freeze, furnace switched between T_{fp}, $T_{\text{fp}} - 0.5$ K, and $T_{\text{fp}} - 1.0$ K) as well as for an induced freeze with furnace temperatures of $T_{\text{fp}} - 0.5$ K and $T_{\text{fp}} - 1.5$ K, respectively. The bottom part of the diagram has been marked because of the above-mentioned uncertainty of 50 μK which corresponds to an uncertainty of μ_{furnace} of 5×10^{-5}. The comparison of the induced and the non-induced freezes in this diagram allows three different conclusions.

The first is an explanation why the maximum of an induced freeze is the most reproducible point. This point is just the state of the fixed-point transition with minimal μ_{furnace}, i.e., minimum influence of heat conduction to the furnace. In the example shown, this corresponds to 20 μK or less (although with a large uncertainty).

The second is a more detailed understanding of the undesired heat conduction between the furnace and thermometer at the beginning of the non-induced freeze. Interestingly, this influence decreases until μ_{furnace} is as small as for an induced freeze (at the same time or same F, respectively). To explain, there has to be an undesirable heat bridge in the fixed-point cell that diminishes with time. One possibility would be a large supercooled zone in the molten material along the inner tube in the absence of nucleation that has good thermal contact to the cooler upper parts of the cell. However, comparisons with measurements on a very slim cell showed no substantial change; μ_{furnace} diminished only by a factor of about five. In the tested slim cell, the width of the fixed-point material is only 2 mm, which should reduce thermal conduction in the molten material along the axis by more than an order of magnitude. Dendrites, however, are out of the question as an explanation, because their influence should increase μ_{furnace} considerably in a slim cell. As further investigations showed no increase of μ_{furnace} in upper parts of the cell (see Fig. 7), it seems most likely that the phase boundary is not closed at the beginning of a non-induced freeze, even in the bottom part of the cell. Therefore, there is good thermal contact between parts of the molten metal and the furnace with its much lower temperature. Without nucleation, this will lead to local supercooling in the liquid metal and a lower temperature at the thermometer. With further freezing of the metal, the frozen parts will grow while μ_{furnace} decreases until the boundary is closed, which results in a much lower value of μ_{furnace}.

The third is the agreement of the μ_{furnace} for both induced and non-induced freezes, which has been confirmed by measurements on another cell with a different design and fixed-point material. Generally, μ_{furnace} is expected to be smaller for an induced freeze than for a non-induced one over the whole range of F, and not only for the first 20% of the plateau. Our results, however, show no reason to suppose positive effects due to the initiation because μ_{furnace} is essentially equal for both plateau types. Further investigations are in preparation.

The linearity of the curves in Fig. 4 is apparently coincidental, because other fixed-point cells yield different shapes (e.g., the one shown in Fig. 7).

Similar investigations have been done on melts. In general, the influence of heat conduction is of similar magnitude as for freezes. Like the induced freeze, at the beginning of a melt, usually between $F = 0.9$ and $F = 0.6$, the influence of heat conduction is very small, i.e., $\mu_{\text{furnace}} < 10^{-4}$ or $\Delta T_{\text{meas}} < 50\,\mu\text{K}$. In particular, we did not observe a difference between melting plateaux with and without a second (inner) phase boundary. However, melting plateaux are not as reproducible as freezing plateaux, probably caused by the transport of material within the cell, especially near the end of the plateau.

5 Correction and Quasi-adiabatic Conditions

When μ_{furnace} is sufficiently known, correction for the influence of heat conduction is possible. As mentioned above, this correction applies only to the influence of the furnace, while the influence of the temperature of the environment cannot be treated yet. According to Eq. 1, the deviation of the measured temperature from the fixed-point temperature is

$$T_{\text{meas}} - T_{\text{fp}} = \mu_{\text{furnace}}(T_{\text{furnace}} - T_{\text{fp}}) \tag{4}$$

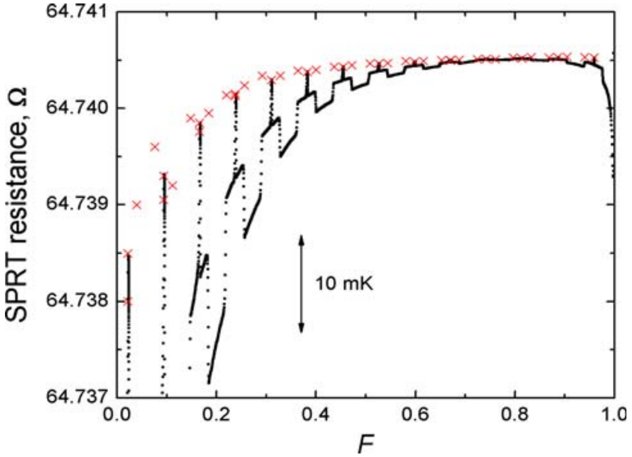

Fig. 5 Diagram shows the agreement between μ_{furnace}-corrected data and measurements under quasi-adiabatic conditions (red crosses) for the same curve as in Fig. 3 (black dots)

It is worth noting that, according to Fig. 4, this correction in most cases depends significantly on F; hence, a static correction is not suitable.

If $T_{\text{furnace}} = T_{\text{fp}}$, evidently there would be no correction needed, but measuring a complete fixed-point plateau for a furnace temperature set constantly close to T_{fp} would take too long, e.g., several days for typical cells if $|T_{\text{furnace}} - T_{\text{fp}}| < 0.2\,\text{K}$. In our measurements, T_{furnace} was set as close as 30 mK to T_{fp}. Thus, the proposed technique of stepwise changes to the furnace temperature allows us to carry out quasi-adiabatic measurements.

Using the same data as before (i.e., the temperature values indicated by the encircled points in Fig. 1), applying the correction (using μ_{furnace}, see Fig. 4) yields the data points in Fig. 5 identified by crosses. The good agreement between the corrected data and the quasi-adiabatic measurements validates the correction method.

It is apparent that the shape of the fixed-point plateau changes vastly by applying the correction, also when the temperature values are drawn as a function of 1/F, as in Fig. 6. For this diagram, a fixed-point realization following standard procedures (i.e., an induced freeze of a zinc fixed-point cell in continuous operation, where the furnace is constantly set to $T_{\text{fp}} - 1\,\text{K}$) is compared with data that are μ_{furnace}-corrected. These data are derived first from the above mentioned non-induced freeze with T_{furnace} switching between T_{fp}, $T_{\text{fp}} - 0.5\,\text{K}$, and $T_{\text{fp}} - 1.0\,\text{K}$ (●), and second from an induced freeze of the same cell with T_{furnace} of $T_{\text{fp}} - 0.5\,\text{K}$ and $T_{\text{fp}} - 1.5\,\text{K}$, respectively (▲). While the corrected data of the latter two measurements are in very good agreement, the slope of the standard fixed-point measurement (i.e., in continuous operation) differs significantly. This is of special importance as the plateau shape has often been used to obtain some kind of information about the content and segregation of impurities by fitting the temperature plateau as a function of $1/F$ [8,11].

If the temperature depression of the uncorrected data, which is mostly due to thermal effects, is treated as induced by impurities, an extrapolation could obviously mislead to an overestimation of the impurity content of a fixed-point cell, different from that

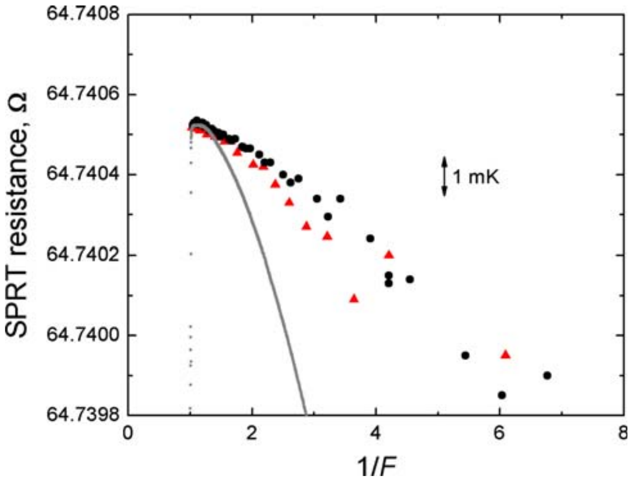

Fig. 6 Typical plateau of an induced freeze of a zinc cell for $T_{\mathrm{furnace}} = T_{fp} - 1.0\,\mathrm{K}$ in comparison with μ_{furnace}-corrected data of two measurements. ▲—induced freeze, furnace set to $T_{\mathrm{fp}} - 0.54\,\mathrm{K}$ and $T_{\mathrm{fp}} - 1.5\,\mathrm{K}$; ●—non-induced freeze, furnace set to T_{fp}, $T_{\mathrm{fp}} - 0.5\,\mathrm{K}$, and $T_{\mathrm{fp}} - 1.0\,\mathrm{K}$

in [10]. Hence, if the slope of a temperature plateau is to be used, the influence of heat conduction has to be considered first. This, however, does not bring into question the fixed-point measurement procedure at all. Indeed, defining the fixed-point temperature in terms of the plateau's maximum is the same for all three curves and the correction term according to Eq. 4 would be smaller than 20 µK.

Comparing Eqs. 2 and 4, the correction proposed here, in effect, corresponds to an extrapolation from measurements with different furnace temperatures to adiabatic conditions, which has been done before, e.g., [11]. Therefore, it is worth noting the difference here. Typically, the plateau data are first fitted to a function of F (e.g., as proportional to $1/F$) and, afterward, the results are extrapolated to $T_{\mathrm{furnace}} = T_{\mathrm{fp}}$. According to the procedure recommended here, the extrapolation of the data to $T_{\mathrm{furnace}} = T_{\mathrm{fp}}$ is done first. Obviously, the results differ in many cases, if the fit to an ideal curve is done afterward.

Admittedly, this should preferably be done only if μ_{ext} (the influence of the heat exchange with the environment, which corresponds to heat conduction to the upper parts of the fixed-point cell) can be neglected. Just as for μ_{furnace}, we expect μ_{ext} to increase at the end of the plateau, and therefore, instead of enriched impurities, an increasing contribution of $\mu_{\mathrm{ext}}(T_{\mathrm{ext}} - T_{\mathrm{fp}})$ is responsible for the temperature depression in the corrected plateau shape (e.g., Fig. 5). A comparison of this remaining depression with the correction done for μ_{furnace} indicates that μ_{ext} is typically much smaller than μ_{furnace}.

Similar to the correction of a plateau, immersion profiles can also be corrected. In this case, the temperature decrease consists of three different components: (a) the hydrostatic-head effect, (b) the thermal influence belonging to μ_{furnace}, and (c) the one belonging to μ_{ext}. If we assume the hydrostatic head to be known, μ_{ext} could be calculated by taking the difference of the real immersion profile [12] and the two men-

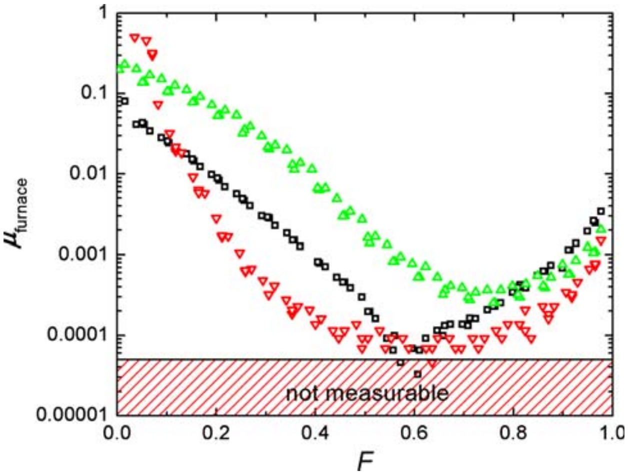

Fig. 7 Penetration ratio as a function of the molten fraction F in a zinc fixed-point cell with a special design for different immersion depths. (thermometer at the bottom of the re-entrant tube (□), 5 cm less immersed (▽), and 10 cm less immersed (△)

tioned corrections (thermal effect of the furnace and hydrostatic-head effect). This, of course, would no longer provide confirmation of the hydrostatic-head effect. However, the separation of heat conduction to the furnace (μ_{furnace}) and heat conduction to the environment (μ_{ext}) is an improvement, because much of the behavior of μ_{ext} will be like that of μ_{furnace} because of their similar nature.

6 Optimization of Cell Designs and Furnace-Temperature Profiles

Since there is a verifiable influence of heat conduction, it seems advisable to optimize the equipment as far as possible to keep the necessary correction small. Obviously, and as mentioned in the first part, a good fixed-point realization is one with small μ_i's. As these μ_i's are not constant, but functions (e.g., $\mu_i(F)$), an overall minimization is probably not possible, but the design goals have to be decided first. The best available fixed-point realization would require a minimization of these μ_i's at the time of the fixed-point measurement, i.e., at the maximum of the freezing plateau, although a long plateau could be preferred instead.

In contrast to the obvious, but laborious, trial-and-error procedure to find a particular suitable cell design, the procedure described in this paper even allows for an estimation of specific weak points of a cell design. As an example, Fig. 7 shows μ_{furnace} for different immersion depths of the thermometer in a zinc cell with a sub-optimal design. In this case, the distance between the tip of the inner tube and the graphite crucible is too small and this part of the cell is completely frozen earlier than the remaining parts of the cell. Therefore, μ_{furnace} increases much earlier at the bottom than in the upper parts of the cell. However, if the thermometer is insufficiently immersed, heat conduction to the top end of the cell prevails, as is also shown.

Such an optimization of a cell design is necessarily restricted to the specific characteristics of a given furnace and also to the fixed point. If, conversely, the fixed-point cell design is given, then the furnace-temperature profile can be measured and likewise optimized, provided that control of the furnace-temperature gradient is provided.

7 Effects Related to Impurity Segregation

Still unproven is the presumption that the so-called diffusion-related effects are negligible, which is very important for the correctness of the work shown, though it seems very likely in view of the good consistency of the measurements with the model. Furthermore, if diffusion-related effects, i.e., the influences of impurities, have a considerable impact, there should have been some differences between measurements with different overall phase-transition rates, i.e., in Fig. 3, the curves of continuous and stepwise freezing should differ from each other, and the two curves with corrected data in Fig. 6 should be more discrepant. As a final indication, melting plateaux show very similar behavior even though an enrichment of impurities cannot be expected in this case. However, further investigations on this matter are planned.

8 Conclusion

In this paper, a procedure to determine the influences of heat conduction on a fixed-point cell has been presented, which is based on measuring the change of the temperature in the fixed point when switching the furnace temperature. For this purpose, a quantitative measure of the quality of a fixed-point cell with respect to the undesired influences of heat exchange with the furnace and with the environment has been proposed. If this so-called penetration ratio is known, a correction can be applied. Although this correction was shown to be less than $20\,\mu\text{K}$ for the maximum of an induced freeze of a well-designed fixed point, the influences of heat conduction dominate the shape of the remaining freezing plateau. As a consequence, the use of the maximum of the freezing curve as recommended by CCT-WG1 [2] is not only the best estimate of the liquidus temperature in order to minimize the influence of impurities but also the best choice to minimize the influence of heat conduction on the measured fixed-point temperature. If, however, the whole plateau is evaluated, thermal effects must be taken into account.

For a non-induced freeze, it has been shown that application of the correction can yield a fixed-point temperature as reliable as for the induced freeze. An alternative is the demonstrated possibility to carry out measurements under quasi-adiabatic conditions. Beyond that, the presented procedure is suitable to optimize both fixed-point cell designs and furnace-temperature profiles and to obtain a better understanding of the formation and location of the phase boundary in fixed-point cells.

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