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COMPARISON OF DIFFERENT METHODS OF FIXED-POINT TEMPERATURE EVALUATION

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Abstract – The estimation of the fixed-point temperatures T_{ph} from measured plateau curves can be carried out using different mathematical methods. Depending on the method used and the size of the fixed-point cell, different systematic deviations and reproducibilities of the calculated temperatures arise. They typically develop during the evaluation of measurements from small fixed-point cells. Thus the phase transformation temperatures of miniaturised fixed-point cells with zinc of different purities were measured and five different methods were compared.

Keywords: fixed-point evaluation

1. INTENTION

Miniature fixed-point cells (MFPC) made of aluminium oxide ceramics and integrated into thermometers can be used for in-situ calibration in industrial processes and power plants [1]. These cells consist of a small crucible, filled with a fixed-point material, where a temperature sensor is inserted (fig. 1). For our measurements we used zinc as the fixed-point material and the sensor was a mineral-insulated Pt100 resistance thermometer. It is inserted into a capillary tube that ensures a highly reproducible positioning of the thermometer in the fixed-point cell. The cell itself is surrounded by a heating element, which can be used to heat up the fixed-point cell above the measured process temperature and induce the melting or freezing of the fixed-point material independent of the process temperature.

Because the size of the MFPC must be relatively small due to practical application conditions (fig. 2) and therefore only a small amount of fixed-point material can be contained within the cell, the plateaux occurring during phase transitions within the course of measuring temperature are significantly shorter and show a larger slope compared to standard fixed-point cells.

The compact design also causes a tight thermal coupling between the sensor in the MFPC and the measurement medium. Because of this, heat dissipation effects can occur which deform the fixed-point plateau and affect the resulting fixed-point temperature. Additionally, measurement distortion can arise due to electromagnetic interference common in industrial environment, which further increases the measurement uncertainty of the sensor in the MFPC.

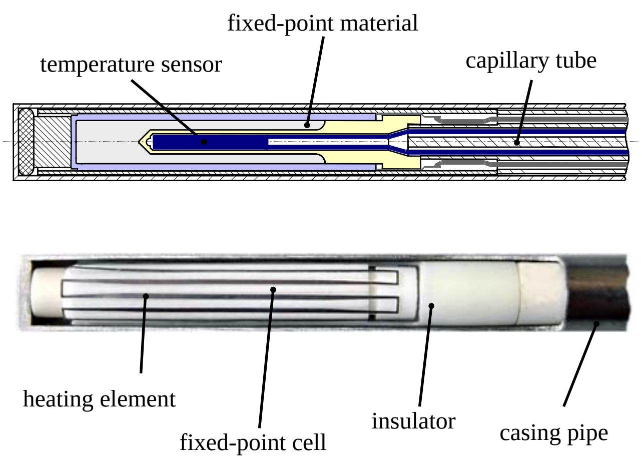

Fig. 1. Sectional view of a thermometer with an integrated fixed-point cell.

These various influencing factors make it important to use dependable methods to determine the fixed-point temperature from the plateau’s shape, which are necessary to allow the calculation of well-reproducible points in the curve of the plateau. Using example laboratory measurements with MFPCs our goal here is to show which measurement deviations and reproducibilites for the determination of fixed-point temperature arise using various evaluation algorithms. In order to investigate the influence of different plateau shapes on the evaluation methods, two MFPCs containing different zinc purities were compared with respect to the measurement and evaluation results yielded during their use.

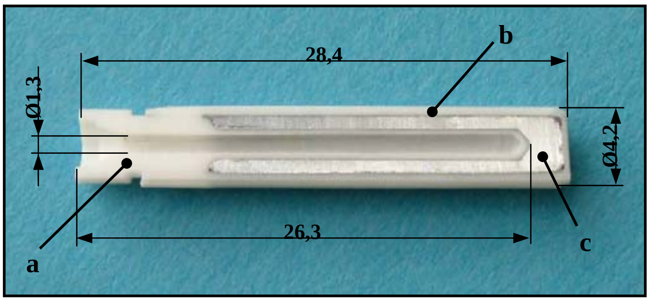

Fig. 2. Sectional view of a zinc fixed-point cell (a- inner crucible, b- exterior crucible, c- fixed-point material).

2. MEASUREMENT SETUP

An MFPC containing 648 mg zinc with 4N purity (99.99 %) as well as one containing 642 mg zinc with 6N purity (99.9999 %) were placed together inside an aluminium oxide calibration block into a tubular furnace and were tempered using a cyclical heating sequence. The oven temperature was varied using ramp-shaped heating rates from 0.01 K/min to 0.1 K/min from 410 °C to 430 °C. The MFPCs' inner-chamber temperatures were recorded at set intervals using an industrial Mineral Insulated Metal Sheathed Pt100 resistance thermometer, which was calibrated with it accompanying measurement chain using a standard zinc fixed point. The active sensor length is 5 mm with an outer diameter of 1 mm. Also, a positioning system assures a defined mechanical and thermal contact between the fixed-points cell and the sensor. The resistance measurements for the Pt100 sensor do take into consideration both self-heating and parasitic thermal voltages, lead resistance and sensor drift.

Both miniature fixed-point cells were taken through 65 solid-liquid and liquid-solid phase transitions. During this process distinctive melting and freezing plateaux were recorded, but in which the beginnings of the melting plateaux and the ends of the freezing plateaux for the 4N cell showed clear slurring due to the impurities compared to the 6N cell. Furthermore, the 4N melting plateaux exhibited a higher slope. Figures 3 and 4 give a comparison of typical examples of phase transition plateaux of both cells.

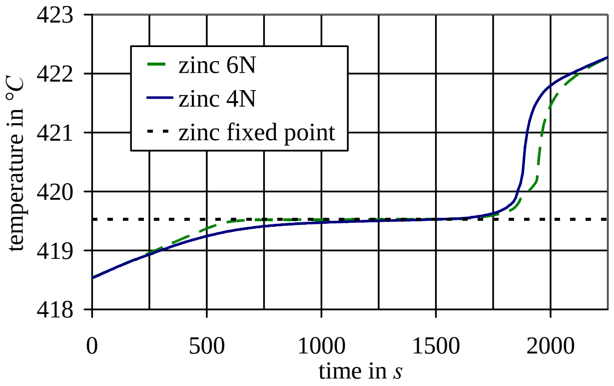

Fig. 3. Measured melting plateaux.

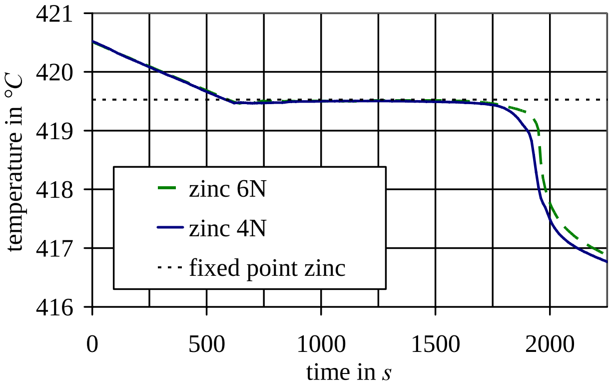

Fig. 4. Measured freezing plateaux.

3. DESCRIPTION OF THE FIXED-POINT EVALUATION METHODS

Various mathematical methods are used in differential thermal analysis and the fixed-point calibration to determine the phase transition temperature T_{ph} from the measured melting and freezing temperature curves. Five of these methods were selected and adapted to the application discussed here. The goal of the method in each case is to find a robust and reproducible temperature point in the plateau, which can be drawn upon for the characterisation of the phase transition process as well as for determining an estimated value for T_{ph}. These method-specific fixed-point temperatures are indexed according to the calculation methods. Suitable plateau points have proven to be the extrapolated plateau starting point T_b, the extrapolated plateau ending point T_e, the plateau inflection point T_i or the plateau maximum value T_m, the most-often occurring measurement value T_d within the plateau's range and the point of the minimum average plateau slope T_s (see fig. 5a). Of course these temperatures deviate systematically from T_{90} due to heat dissipation errors, impurities in the fixed-point material and similar influencing factors. It is therefore necessary to include these in a separate measurement uncertainty budget (see [2]). The mathematical methods used to determine these points will be explained in the following sub-sections.

3.1. Determination of the extrapolated plateau starting point T_b using straight-line approximation of the plateau curve

The beginning and end of the course of a phase transition are strongly influenced among other things by thermal lag and by effects stemming from thermal inhomogeneities and impurities. For this reason the measured temperature significantly deviates from the expected starting and ending temperature in the respective plateau region. However, an estimated value for the beginning of the melting process can be determined by using areas within the plateau which are largely free of disturbances as the basis for two approximation lines *a* and *b* (see fig. 5a). The intersection of these lines represents the extrapolated plateau starting point T_b [2]. The approximation lines are determined using the least squares method.

3.2. Determination of the extrapolated plateau end point T_e using straight-line approximation of the plateau curve

Equivalent to the method shown in 3.1, the temperature T_e is determined as the intersection point of lines *b* and *c*.

3.3 Determination of the inflection-point temperature T_i of the melting curve or the maximum temperature T_m of the freezing curve using polynomial approximation

By taking a section of the melting plateau curve around the central point of the plateau region (appr. 50 % of the material has melted) and describing this section using a third-order polynomial [3], the point of inflection of this polynomial (called T_i) can be considered a well- reproducible approximation of the melting point. The plateau region between the already determined points T_b and T_e have proved to be suitable. Because the freezing plateau dips below the transition temperature, these plateaux exhibit a shape which can be modelled with a second-order polynomial. The maximum value T_m of this polynomial can be considered an estimated value of the freezing temperature.

3.4. Determination of the temperature T_s at the point of minimum plateau slope

Regions often occur during melting and freezing plateaux in which the plateau exhibits an almost constant slope. Measurements behaving this way do not allow the robust determination of the inflection point or the maximum value (as described in 3.3) with little error.

It is better to extract the section of the plateau exhibiting the minimum constant slope (if necessary after smoothing the values with an appropriate filter, such as a moving average filter) and calculating the mean of the individual temperature values in this section. The temperature T_s determined in this way has proved to be extremely reproducible.

3.5. Determination of the maximum temperature T_v of the measurement value distribution (histogram method)

Taking the temperature values measured during the phase transition, dividing them into classes of width ΔT and determining the number of occurrences n of each class, we obtain the histogram $T(n)=f(n)$ as shown in fig. 5b [4]. The class width ΔT must be adapted to the resolution of the thermometers used and the number of available measurement values. A distinct maximum value T_d of the distribution function $T(n)$ can be determined with the optimal selection of ΔT. However, this method values for plateaux with wide areas of constant slope. Also, the uncertainty of this method is greatly influenced by the selected class width and the measurement noise.

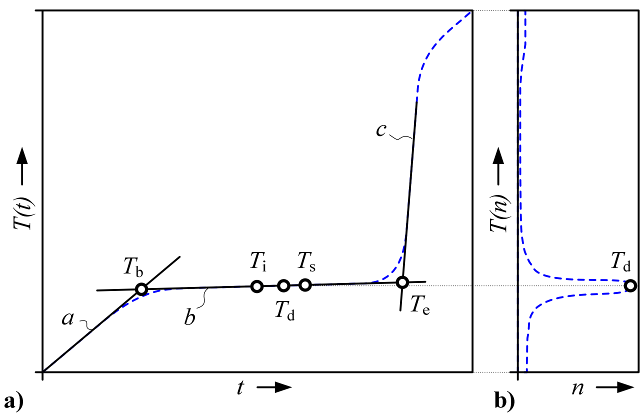

Fig. 5. Schematic diagram of a melting plateau and the estimated reference temperature points.

4. RESULTS AND INTERPRETATION

4.1. Melting

Figures 6 and 7 show the melting plateaux found using the different methods for the MFPCs described above. Looking first at plateau points for the cell filled with 4N zinc, we can clear see that the temperatures T_w, T_v and T_a are only slightly influenced by the heating rate during the phase transition. The average temperature values are located around 419.510 °C – approximately 7 mK below the ITS-90 zinc fixed-point temperature, as would be expected from a fixed-point cell with the impurities of 4N zinc. The standard deviation of the determined "virtual" fixed points is 6 mK to 8 mK for the lowest heating rate and climbs to 12 mK to 20 mK for the highest heating rate (table 1).

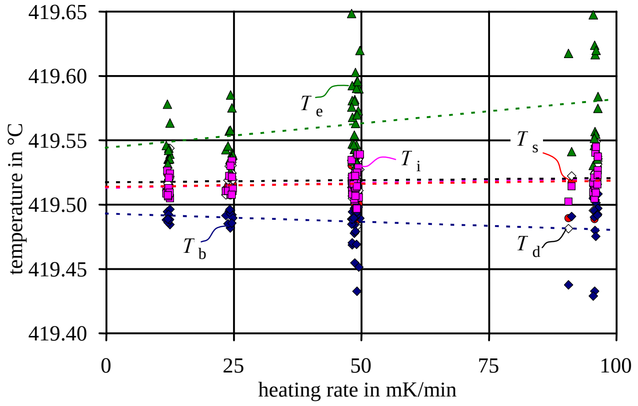

Fig. 6. Results of the five methods applied to melting plateaux of a cell filled with 4N zinc

The evaluation methods for T_i, T_d and T_s yield almost equal-valued results. The smallest variances for this specific 4N zinc plateau shape can be obtained using the inflection-point method. The systematic temperature deviations among the various methods are in the area of a few millikelvins.

The extrapolated plateau end temperature T_e and the extrapolated plateau starting temperature T_b are heavily influenced during the phase transition by the heating rate and therefore by the surrounding oven. Because of this dependency T_b and T_e appear to be less suitable as a measure of the phase transition temperature. However, inferences can be drawn from their position regarding the existence of impurities or heat dissipation errors.

Table 1. Analysis results of a melting plateau using a 4N zinc MFPC

Cool. rate in mK/min	T_i	T_d	T_b	T_e	T_s
Standard deviation of the temperature points in K (k=1)					
12	0.008	0.009	0.006	0.015	0.006
24	0.009	0.007	0.008	0.018	0.008
46	0.010	0.012	0.017	0.030	0.011
95	0.012	0.017	0.026	0.038	0.016
Mean of the temperature points in °C (T_{90}(Zn)=419.527 °C)					
12	419.513	419.521	419.491	419.545	419.515
24	419.516	419.518	419.494	419.548	419.517
46	419.517	419.517	419.485	419.568	419.515
95	419.520	419.522	419.482	419.575	419.519

Table. 2. Analysis results of a melting plateau using a 6N zinc MFPC

Cool. rate in mK/min	T_i	T_d	T_b	T_e	T_m
Standard deviation of the temperature points in K (k=1)					
12	0.003	0.004	0.003	0.005	0.002
24	0.004	0.005	0.005	0.010	0.004
46	0.007	0.008	0.009	0.012	0.007
95	0.008	0.009	0.012	0.022	0.008
Mean of the temperature points in °C (T_{90}(Zn)=419.527 °C)					
12	419.525	419.524	419.514	419.539	419.524
24	419.525	419.524	419.514	419.539	419.524
46	419.520	419.521	419.508	419.536	419.520
95	419.524	419.525	419.506	419.548	419.525

If we compare these results with the evaluation of the 6N zinc cell, we see that the calculated temperature points lie nearer to each other due to the flatter plateau shape, thus achieving a reduced standard deviation. Because of the higher material purity T_i, T_d and T_s are on average 419.524 °*C*, giving a deviation of only -3 mK from T_{90}(Zn). Even T_e and T_b show a significantly smaller systematic deviation and a lower dependency on heating rate than is the case for the cells with less pure zinc.

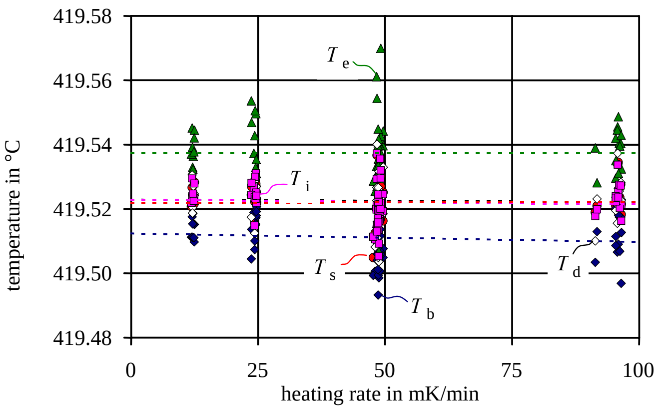

Fig. 7. Results of the five methods applied to melting plateaux of a cell filled with high-purity zinc

4.2. Freezing

In contrast to the melting process, the analysis of freezing delivers remarkably similar results using all five methods. The data show that the determined "virtual" fixed-point temperatures decrease with increasing cooling rate. This effect arises for both cells equally due to the small amount of fixed-point material being used, which only releases a small amount of solidification energy. This amount is not sufficient to attain the actual phase transition temperature T_{ph} within the cell.

If for example we extrapolate the plateau maximum T_m to a cooling rate of 0, the idealised values deviate from T_{90}(Zn) by -12 mK for the 6N cell and even up to -23 mK for the 4N cell. It is also conspicuous that the systematic deviations of the freezing plateaux among the various methods are smaller than among the results for the melting plateaux. This is also caused by the form of the freezing plateau. Because the temperature behaviour of the solidification process is often symmetrical near the maximum value and it shows a very small rate of change (see fig. 3), the fitted lines used to determine T_e and T_b in the region of the plateau run virtually horizontally. Because of this T_d also lies near these values.

Only the determination of the actual plateau maximum T_m yields slightly higher temperatures, while T_s delivers a virtual phase transition temperature which is too low again caused by systematic influences (mainly from the averaging at and near the plateau maximum). The variance of the calculated temperatures is identical, both for the 4N and 6N cells as well as for the various methods. The standard deviation of the individual methods amounts to 4 to 8 mK at the lowest heating rate and from 24 mK to 28 mK at the highest heating rate.

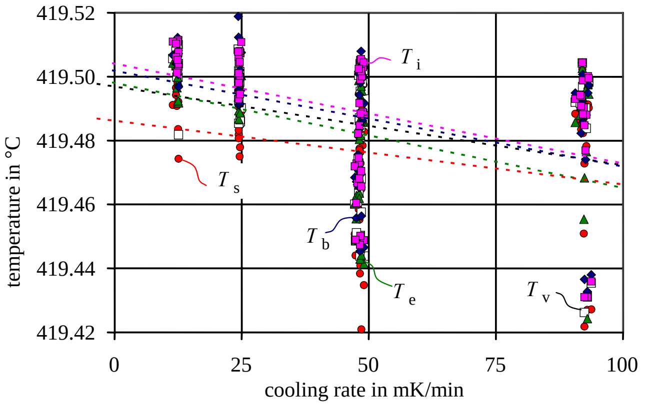

Fig. 8. Results of the five methods applied to melting plateaux of a cell filled with 4Nzinc

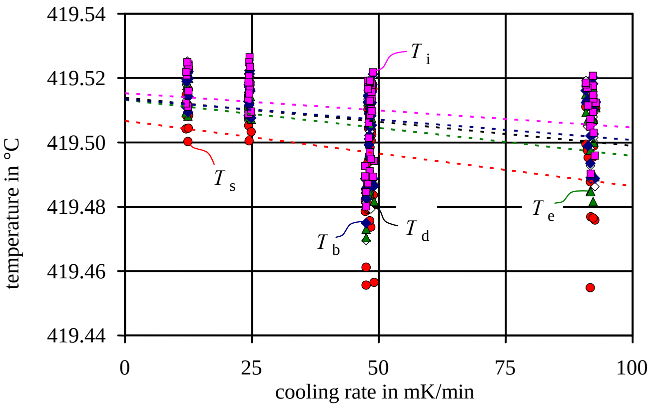

Fig. 9. Results of the five methods applied to melting plateaux of a cell filled with high-purity zinc

5. CONCLUSIONS

On the basis of the analysis of melting and freezing processes in miniature fixed-point cells, five methods were introduced for determining approximate values for the phase transition temperature. We were able to show that the various methods are affected by a variety of factors. The general shape of the phase transition and the number of available measurement values both have an especially large influence on the systematic measurement deviations and the resulting variance of the calculated virtual fixed-point temperatures. Depending on the application it is sensible to utilise several methods to calculate the fixed-point value for the same phase transition process. This makes it possible to identify the most reproducible method and yields in most cases additional information regarding the deterioration of the fixed-point material, its impurities and the thermal coupling of the fixed-point cell or rather the sensor contained within in and their surroundings. However, which method actually yields the best approximation of the fixed-point temperature T_{ph} must be determined on a case-by-case basis in a separate evaluation of measurement uncertainty. For this, the systematic deviations of the evaluation method must also be taken into account. Regarding the systematic errors it still appears to be sensible to favour methods which analyse the middle plateau region. This section is influenced significantly less by impurities or the thermal environment of the fixed-point cell compared to the beginning and end of the plateau.

Through the analysis of miniature fixed-point cells filled with 4N and 6N zinc, we were able to show that very reproducible fixed-point temperatures could be obtained using the melting plateaus of MFPCs. The freezing plateaus, however, proved to be less useful for calibration purposes due to the variance of the virtual fixed-point values and the systematic temperature deviations.

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