Int J Thermophys (2007) 28:1983–1992
DOI 10.1007/s10765-007-0268-x

Melting Temperatures of Eutectic Fixed-Point Cells Usable for the Calibration of Contact Thermometers

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Published online: 10 October 2007

Abstract The objective of the present investigation was the determination of the melting temperatures of the eutectic compounds Fe–C, Co–C, and Ni–C. Six eutectic fixed-point cells of the Physikalisch-Technische Bundesanstalt (PTB) (Fe–C1, Fe–C2, Co–C1, Co–C2, Ni–C1, and Ni–C2) and two cells of the Brazilian National Metrological Institute (Inmetro) (Fe–C1V and Ni–C1V), useable for the calibration of contact thermometers, were investigated. Their melting temperatures were calculated by extrapolation of the emf-temperature characteristics of four stable Pt/Pd thermocouples, which were calibrated at the eutectic fixed points and at conventional fixed points of the International Temperature Scale of 1990 (ITS-90). On the basis of the eight eutectic fixed-point cells and seven independent calibration runs, the melting temperatures of the Fe–C, Co–C, and Ni–C eutectics resulted in 1153.67 ± 0.15°C, 1323.81 ± 0.27°C, and 1328.48 ± 0.20°C, respectively, with expanded uncertainties corresponding to a coverage factor of $k = 2$.

Keywords Contact thermometers · Eutectic fixed points · Extrapolation method · Inflection point · Melting temperatures · Platinum/palladium thermocouples

1 Introduction

The freezing point of copper 1084.62°C is the fixed point of the International Temperature Scale of 1990 (ITS-90) having the highest phase-transition temperature. At higher

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temperatures, only the melting point of palladium 1554.8°C and the melting/freezing point of platinum 1768.2°C are available as secondary fixed points [1] for the calibration of thermometers, but with limited practicability. With the implementation of high-temperature fixed points of eutectic metal–carbon or metal carbide–carbon compounds, this situation changed at the end of the 1990s. These new fixed points were, due to their high melting temperatures up to 3,185°C, HfC-C [2–5], constructed mainly for non-contact applications. Recently, their potential for the calibration of contact thermometers, especially of thermocouples, has become evident [6–8].

The estimated melting temperatures of the metal carbon eutectics Fe–C 1,154°C, Co–C 1,324°C, and Ni–C 1,329°C are within the temperature range bracketed by the freezing point of Cu and the melting point of Pd. If their exact values were known, the calibration uncertainties of thermocouples at temperatures above 1,100°C could be significantly reduced. Above the freezing point of silver 961.78°C, the ITS-90 is defined by radiation thermometers, which are usually used in a horizontal configuration. Fixed-point cells usable for the calibration of contact thermometers, however, are usually used in a vertical position and are, in general, not suited to being used in a horizontal position because of the higher risk of breakage of the thermometer well.

For the investigation reported here, four stable Pt/Pd thermocouples were calibrated in the temperature range between 0 and 1,100°C at conventional fixed points of the ITS-90, and were measured at the three eutectic fixed points of interest. The results of the measurements at the conventional fixed points were extrapolated to calculate the melting temperatures of the Fe–C, Co–C, and Ni–C eutectic fixed-point cells by comparing the directly measured electromotive voltages (emfs) at these fixed points with the extrapolated emf-temperature function.

2 Eutectic Fixed Points

The use of metal–carbon compounds as fixed-point materials in graphite crucibles reduces the risk of these materials being contaminated by the material of the crucible, as graphite is one of the eutectic fixed-point components. On the other hand, the chemical affinity between the crucible and the fixed-point material, together with their different thermal expansion coefficients, can lead to a breakage of the graphite crucibles. Therefore, double-walled crucibles with rounded, rough edges are used. The latter should reduce the sticking of the eutectic material to the graphite of the crucible and, thereby, reduce the risk of breakage. Figure 1 shows a schematic diagram of a eutectic fixed-point cell usable for the calibration of contact thermometers. The dimensions of the eutectic fixed-point cells investigated at PTB and Inmetro are listed in Table 1.

In contrast to the conventional fixed points of pure metals, metal–carbon eutectic fixed points are characterized by a different melting and freezing behavior. The melting and freezing temperatures differ from each other by some tenths of a degree, both plateaux are less flat than the corresponding plateaux of pure metals, and the freezing temperature depends on different parameters, i.e., on the freezing rate, on the furnace temperature offset from the freezing plateau, and on the heat treatment of the fixed-point cell before completing the freeze. Therefore, according to the consensus of the

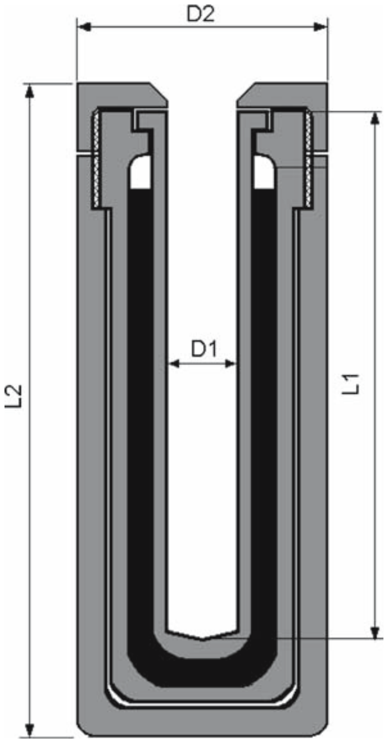

Fig. 1 Schematic diagram of a eutectic fixed-point cell

Table 1 Dimensions of the eutectic fixed-point cells (see Fig. 1)

	D1[a] (mm)	D2[b] (mm)	L1[c] (mm)	L2[d] (mm)
PTB cells	8	34	95	117
Inmetro cells	8	40	100	123

[a] Inner diameter of the thermometer well
[b] Outer diameter
[c] Inner length of the thermometer well
[d] Overall length

temperature community and based on the high reproducibility found for the inflection point of a melting curve, the corresponding emf of this point of the melting curve is used to define the eutectic phase-transition temperature. Figure 2 shows a typical melting and freezing curve of a Ni–C eutectic, measured by means of a Pt/Pd thermocouple.

The purity of the graphite of the eutectic cells of PTB which were delivered by Schunk Kohlenstoff GmbH was 5N5, with a density of $1.9\,g \cdot cm^{-3}$. The nickel, cobalt, iron, and graphite powders used to fill the crucibles were provided by Alfa Aesar and had a purity of 99.996% (Ni), 99.998% (Co and Fe), and 99.9999% (graphite). The metal powders were each mixed with the graphite powder at approximately 3.0 mass% carbon for Ni–C and at approximately the eutectic composition of the

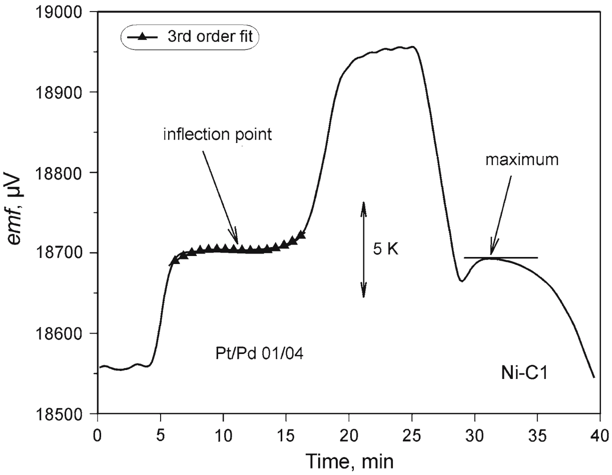

Fig. 2 Typical melting and freezing curve of eutectic compounds

Co–C (2.6 mass% carbon) and Fe–C (4.2 mass% carbon) alloys. Two cells of each material were filled with the powder mixture at PTB, heated for about 40 min in an argon atmosphere to a temperature about 15 K above the eutectic melting temperature, and then cooled to room temperature. This procedure was repeated until the crucibles were completely filled (5–9 runs). The eutectic fixed-point cells are designated Fe/Co/Ni–C1 and Fe/Co/Ni–C2.

The Inmetro cells were fabricated with graphite of unspecified purity having a medium grain size of 12 μm, a maximum ash residue of 10 ppm, and a declared and measured density of $1.8\,\mathrm{g \cdot cm^{-3}}$. The graphite for Fe–C1V was supplied by Carbono Lorena and for Ni–C1V by Seecil Carbon Technologies Ltd. The metal and graphite powders needed to fill the Inmetro cells that were also provided by Alfa Aesar and had the same purity as given above. The mixing and filling procedures were the same as those applied at PTB.

3 Experimental Details

Four Pt/Pd thermocouples were constructed at PTB and Inmetro, two at each laboratory, according to a procedure described elsewhere [7]. Prior to calibration, the thermocouples were annealed at a temperature of 1,340°C for about 120 h to achieve an adequate thermoelectric stability (<1 μV). This was checked by repeated measurements at the freezing points of copper or silver. Their thermoelectric homogeneity was checked by immersion profile measurements at the freezing point of silver. The thermocouples and the eutectic fixed-point cells were used extensively for other purposes before starting the investigations presented here.

Seven complete calibration runs were performed, six at PTB and one at Inmetro. The measurements started at the Ni–C eutectic, which is the eutectic with the highest melting temperature among the three (Fe–C, Co–C, and Ni–C) investigated here. The

Table 2 Extrapolated melting temperatures of the eutectic fixed-point cells (°C)

TC date[a]	INM 03/03 10/2004	INM[b] 03/03 1/2005	INM 03/03 11/2005	INM 02/05 11/2005	Pt/Pd 01/04 11/2004	Pt/Pd 01/04 11/2005	Pt/Pd 01/05 12/2005
Fe–C1	1153.70	1153.68			1153.56		1153.83
Fe–C2			1153.65	1153.72		1153.65	
Fe–C1V			1153.65			1153.63	
Co–C1	1324.01	1324.0			1323.66		
Co–C2			1323.50	1323.61			1323.85
Ni–C1	1328.52	1328.51	1328.43		1328.45	1328.66	1328.50
Ni–C2			1328.33	1328.51		1328.54	
Ni–C1V			1328.38			1328.39	

[a] Date of the calibration of the corresponding Pt/Pd thermocouple
[b] Calibration at conventional fixed points of Inmetro (all other calibration cycles were performed by using conventional fixed points of PTB)

melting plateaux of the eutectics were realized in an argon atmosphere in the high-temperature furnaces of PTB (HTF-R) [7]. In each calibration run, at least three melting curves were measured for each eutectic fixed-point cell. The freezing plateaux of the conventional fixed points copper, silver, aluminium, zinc, and in some cases, tin, and the melting point of gallium were realized in this order in the two laboratories. The emfs were measured with a Keithley 2182 or an HP 3457A voltmeter at PTB and with an HP 3457A at Inmetro. The reference junctions of the thermocouples were maintained in an ice-point (0°C) cell.

The deviations from the Pt/Pd reference function of the emfs measured at the conventional fixed points were fitted by first-order deviation functions in the temperature range between 0 and 1,100°C. These linear deviation functions were extrapolated to the estimated melting temperatures, T_{es}, of the eutectics: 1,329°C (Ni–C), 1,324°C (Co–C), and 1,154°C (Fe-C), and then used to derive the melting temperatures of the different eutectic fixed-point cells.

4 Results

The melting temperatures obtained by applying the extrapolation method are listed in Table 2 for each of the eutectic fixed-point cells. They agree well, despite the different sensitivities among the thermocouples. For instance, their emf values at the freezing point of Cu are within +2.3 μV (Pt/Pd INM 02/05) and -25.9 μV (Pt/Pd 01/05) of the reference function.

5 Measurement Uncertainty

The melting temperatures of the eutectic fixed points were calculated according to the following equation:

$$T_M = T_{es} + \Delta T \tag{1}$$

The measurement uncertainty of the calculated melting temperatures, T_M, of the eutectic fixed-point cells is caused only by the uncertainty of the temperature difference ΔT. The combined uncertainty is obtained by means of the quadratic sum of the following uncertainty contributions:

(1) uncertainty of the emf–T relationship of the Pt/Pd thermocouples in the temperature range between 0 and 1,100°C due to the uncertainty of the calibration at the conventional fixed points (deviation function);
(2) uncertainty due to the extrapolation of the individual deviation functions to the estimated melting temperatures T_{es};
(3) uncertainty due to the measurement of the Pt/Pd thermocouples at the eutectic fixed points; and
(4) uncertainty due to the reference function of the Pt/Pd thermocouples at the melting temperatures of the eutectic fixed points.

The uncertainties of the measured emfs, E_X, at the conventional and eutectic fixed points were calculated according to

$$E_X = E_X(FP) + \delta E_{RP} + \delta E_{Pl} + \delta E_{HF} + \delta E_{el} + \delta t_0 S_0 + \delta E_H + \delta E_{S-Cu/Ag} E_X(FP)/E_{Cu/Ag}, \quad (2)$$

with E_X(FP) as the emf indicated by the voltmeter. The combined measurement uncertainty of E_X is obtained by summing in quadrature the following uncertainty contributions:

- δE_{RP}: repeatability of the emf measurements;
- δE_{Pl}: selection of the value on the freezing plateau (inflection point at eutectic fixed points);
- δE_{HF}: heat flux effects along the thermocouples;
- δE_{el}: uncertainty of the electrical measurement;
- δt_0: uncertainty of the reference junction temperature t_0;
- δE_{sH}: thermoelectric inhomogeneity; and
- $\delta E_{S-Cu/Ag}$: stability at the freezing points of Cu or Ag.

S_0 is the Seebeck-coefficient at the ice point. Additionally, the uncertainty of the deviation functions has to be included to obtain the uncertainty of the individual emf–T relationships in the temperature range from 0°C to 1,100°C.

The uncertainty of the extrapolation of the deviation functions depends on the accuracy of the approximation, and therefore on the individual thermocouple characteristics, and varies within a temperature equivalent range from 0.03 to 0.14 K. The uncertainty of the measurement at the eutectic fixed-point cells was between 0.05 and 0.06 K. The values of these two uncertainty contributions, together with the uncertainties of the emf–T relationships in the temperature range from 0°C to 1,100°C, are summarized in Table 3. The uncertainty of the reference function at the eutectic fixed points amounts to 0.04 K (Fe–C) and 0.08 K (Co–C and Ni–C). The uncertainty of the melting temperature of a eutectic fixed-point cell for a single calibration run, u_i, can be calculated by the quadratic sum of the four uncertainty contributions mentioned above.

Table 3 Uncertainties of the deviation functions in the temperature range 0–1,100°C, of the extrapolation of the deviation functions and of the calibration at the eutectic fixed points in kelvin for $k = 1$

Thermocouple date[a]		Fe–C		Co–C		Ni–C	
	(1) 0–1,100[b]	(2) Extrapolation[c]	(3) Calibration[d]	(2) Extrapolation[c]	(3) Calibration[d]	(2) Extrapolation[c]	(3) Calibration[d]
INM 03/03 10/2004	0.1	0.03	0.06	0.03	0.06	0.03	0.05
INM 03/03 11/2005	0.15	0.11	0.05	0.11	0.05	0.11	0.05
INM 03/03 1/2005	0.15	0.14	0.05	0.14	0.05	0.14	0.05
INM 02/05 11/2005	0.15	0.08	0.05	0.08	0.05	0.08	0.05
PT/Pd 1/4 11/2004	0.15	0.05	0.05	0.05	0.06	0.05	0.05
Pt/Pd 1/4 11/2005	0.15	0.03	0.05	–	–	0.03	0.06
Pt/Pd 01/05 12/2005	0.15	0.04	0.06	0.04	0.06	0.04	0.06

[a] Date for calibration of the corresponding Pt/Pd thermocouple
[b] Measurement uncertainty of the deviation function in the temperature range between 0°C and 1,100°C, calculated according to Eq. 2 and taking into account the mathematical uncertainty of the approximation of the deviation function
[c] Mathematical uncertainty of the extrapolation of the deviation function at the estimated melting temperatures of the different eutectic compounds
[d] Uncertainty associated with the measurement of the Pt/Pd thermocouples at the different eutectic fixed points according to Eq. 2
(1), (2), (3) Uncertainty contributions (see Sect. 5)

Table 4 Weighted mean temperatures of the eutectic fixed-point cells and their combined uncertainties ($k = 1$)

Fixed-point cell	Temperature (°C)	Uncertainty (K)
Fe–C1	1153.69	0.10
Fe–C2	1153.67	0.11
Fe–C1V	1153.64	0.13
Co–C1	1323.91	0.17
Co–C2	1323.67	0.17
Ni–C1	1328.52	0.11
Ni–C2	1328.47	0.15
Ni–C1V	1328.39	0.15

Table 4 contains the weighted mean melting temperatures of the eight eutectic fixed-point cells, calculated with the p_i as weighting factors, and their combined uncertainties, u_{cell}, for $k = 1$, calculated according to Eq. 3:

$$u_{\text{cell}} = \sqrt{u_{\text{ce}}^2 + u_{\text{dev}}^2 + u_{\text{res}}^2} \tag{3}$$

where $u_{\text{ce}} = \sqrt{1/\sum_{i=1}^{n} p_i}$ and $p_i = 1/u_i^2$. The component u_{dev} is the standard deviation of the mean melting temperatures of the n independent calibration runs (n is between 2 and 6) for each cell. The component u_{res} is the resolution of the measurement method and is identified with the *uncertainty of the reference function of Pt/Pd thermocouples at the eutectic fixed points* [9], whose values are given above. In order to avoid double counting, the uncertainty of the reference function was not included as an uncertainty contribution to calculate the single values of u_i. The mathematical procedure used to calculate u_{ce} assumes that the particular uncertainties u_i are of statistical character only. However, the u_i mainly include type B uncertainty contributions. Therefore, the standard deviation of the mean melting temperature u_{dev} was also taken into account in calculating the uncertainty of each cell.

6 Conclusion

Figure 3 compares the melting temperatures of the eight eutectic fixed-point cells (Table 4) calculated with the extrapolated thermocouple deviation functions to the values determined by radiation thermometry. All temperatures are shown with their expanded uncertainties for $k = 2$. The figure indicates good agreement between the temperatures determined by the two methods. Furthermore, the uncertainties associated with the thermocouple extrapolation method are of the same order as the measurement uncertainties of radiation thermometry in this temperature range.

The small differences found among the melting temperatures of different cells of the same eutectic compounds allow the mean melting temperatures of the three eutectic compounds Fe–C, Co–C, and Ni–C to be used as values for their ITS-90 temperatures. The weighted mean temperatures of the eutectic systems and their expanded uncertainties for $k = 2$ amount to 1153.67 ± 0.15°C, 1323.81 ± 0.27°C, and 1328.48 ± 0.20°C for Fe–C, Co–C, and Ni–C, respectively. The associated uncertainties of the melting

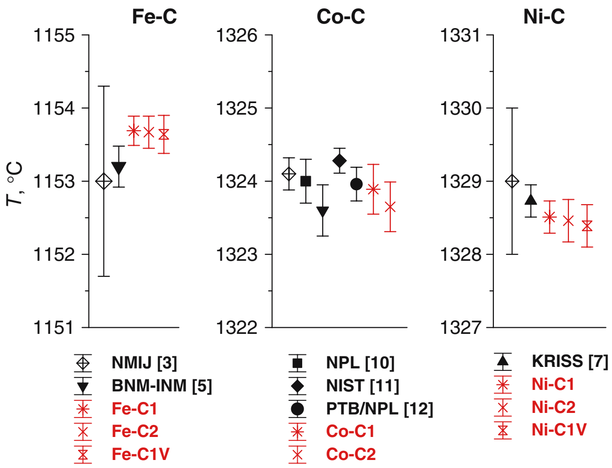

Fig. 3 Melting temperature and expanded uncertainties ($k = 2$) of eutectic fixed points

temperatures of the eutectic compounds were calculated in the same way as the uncertainties of the melting temperatures of the single cells described above, but considering all calibration runs for each eutectic system (Fe–C: 9 runs, Co–C: 6 runs, and Ni–C: 11 runs).

7 Summary

The melting temperatures of eight eutectic fixed-point cells of PTB and Inmetro were determined by extrapolating the emf–T relationships of four Pt/Pd thermocouples, calibrated seven times at conventional fixed points of the ITS-90. The calculated temperatures agree very well with the radiometrically determined temperatures of these eutectic compounds. The results demonstrate the capability of vertical eutectic fixed-point cells used for thermocouple thermometry to disseminate temperatures with uncertainties comparable to those achieved with horizontal blackbody cavities for radiation thermometry, in spite of differences in the design and size of the cells used for contact and non-contact applications.

Acknowledgments This work was supported by the International Bureau of the BMBF at Deutsches Zentrum fuer Luft- und Raumfahrt e.V., Germany, Project-No. BRA 02/030, and by FINEP—Brazil.

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