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On the Use of the Co–C Fixed Point for Calibration of Pt/Pd Thermocouples

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Abstract At INRIM, different Co–C fixed-point cells have been constructed and investigated. Two cells of different design and volume and filled with highly pure cobalt (99.998%) were used to extend the fixed-point calibration of five Pt/Pd thermocouples that had been previously calibrated at the triple point of water and at the fixed points of In, Sn, Zn, Al, and Ag. The calibration at the Cu point was also added during this exercise. Because a previous calibration from 962 °C up to 1,500 °C against the local standard radiation thermometer was available, a comparison was possible with the Co–C fixed-point calibration. Agreement within 0.10 °C was found when the value of 1,324.0 °C, the same value proposed for the Co–C point to be included as a secondary reference point of the ITS-90, was assumed.

Keywords Co–C · Eutectics · Fixed points · Pt/Pd thermocouples

1 Introduction

Because of the paucity of reproducible fixed points above the copper point (1,084.62 °C), the calibration of Pt/Pd thermocouples in their high-temperature range of operation, namely, from about 1,100 °C to 1,500 °C, needs to be carried out by comparison with a primary standard radiation thermometer. This is generally a complicated procedure and, to fully exploit the accuracy of Pt/Pd thermocouples, high-level calibration techniques need to be adopted and specially designed high-temperature furnaces and blackbody cavities must be used. Previous investigations [1,2] were carried out where special care was devoted to arrange and characterize multi-zone blackbody

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furnaces to obtain the best axial uniformity, an essential requirement to ensure that the radiance temperature and the temperature measured by the thermocouple are well matched. The availability of eutectic metal-carbon fixed points below 1,500 °C, for example, Co–C and Pd–C, may be a valuable alternative in order to simplify the calibration procedure and possibly improve the uncertainty level. The use of the Co–C eutectic point may be a significant step forward because, even if the range of operations of the Pt/Pd thermocouples is not completely covered, it allows a calibration procedure to be adopted up to 1,324 °C based entirely on fixed points.

The aim of the present investigation was to experimentally verify the viability of the fixed-point calibration procedure and to compare the results with those obtained by comparison with the radiation thermometer. Because a temperature has not yet been formally assigned to the Co–C eutectic point, a comparison of the two techniques may give useful information.

The paper describes the experimental arrangement to extend the fixed-point calibration to the Cu and Co–C points, shows the measurements results, and discusses them in relation to those obtained with the radiation thermometer.

2 Experimental Arrangement and Measurements

Five Pt/Pd thermocouples, identified as ET, Ea, Ea+, I1, and I2, were constructed and calibrated at the fixed points of Ag, Al, Zn, Sn, In and at the triple point of water at IMGC (now INRIM). Details of their construction, investigations of stability and homogeneity, and fixed-point calibration data can be found in [3]. The thermocouples were manufactured from Pt and Pd wires of different purities and from different suppliers, as summarized in Table 1. Thereafter, the thermocouples were calibrated by comparison with the local standard radiation thermometer in the temperature range from 962 °C to 1,500 °C [2]. For this purpose, a horizontal multi-zone high-temperature GERO furnace provided with a specially designed and IMGC-fabricated blackbody cavity was used as a transfer source. A detailed description of the furnace and its characterization is reported in [2].

The original calibration was extended in the present investigation to the Cu and Co–C points. The fixed-point cells and furnaces used for the calibration are described in the following subsections.

Table 1 Characteristics of the thermocouples

Thermocouple identification	Pt wire (manufacturer, purity)	Pd wire (manufacturer, purity)
ET	Engelhard, 99.99%	Engelhard, 99.95%
Ea	Engelhard, 99.99%	Alfa Aesar, 99.9%
Ea+	Engelhard, 99.99%	Alfa Aesar, 99.99+%
I1	Ishifuku, 99.999%	Ishifuku, 99.95+%
I2	Ishifuku, 99.999%	Ishifuku, 99.95+%

2.1 Fixed-point Cells

The calibration at the Cu point was performed using the sealed cell Cu JM-1 described in [4].

Two different cells were used for the measurements at the Co–C point. The first one was the *Co_4N8_big* cell described in [5]. The outer diameter and total length of the crucible were 42 mm and 110 mm, respectively. The inner diameter of the thermometer well was 8.5 mm, and the immersion depth was 88 mm. The consequent inner volume of the crucible was 43 cm^3, and the shell thickness of the eutectic ingot was 6.5 mm. All crucible components were made from high-purity graphite with less than 10 ppm ash content.

Because the cell was designed to be used with both thermocouples and radiation thermometers, it was not optimized for a specific application and the resulting length of the thermometer well could be critical for contact thermometry applications. Another cell was then constructed, the *Co_4N8_long*, with the same outer diameter, 42 mm; and inner diameter of the thermometer well, 8.5 mm; but with increased total length and effective immersion depth, 210 mm and 135 mm, respectively. The inner volume was reduced to about 25 cm^3 and, consequently, the resulting shell thickness of the ingot was reduced to 2.5 mm. A filling procedure was followed which was similar to that adopted in [6] and consisted of fitting the thermometer well into the crucible when the latter had been filled with the cobalt–graphite powder mixture after it had completely melted. Unlike the method of successive fillings used for the *Co_4N8_big* cell, a limited number of runs were necessary to complete the filling procedure, i.e., two runs instead of ten or more with the former method. In consideration of the limited useful space of 2.5 mm between the thermometer well and the crucible, a special design of the bottom of the thermometer well was devised to allow, and force, the latter to be vertically introduced into the crucible (see the detail in the enlargement in Fig. 1).

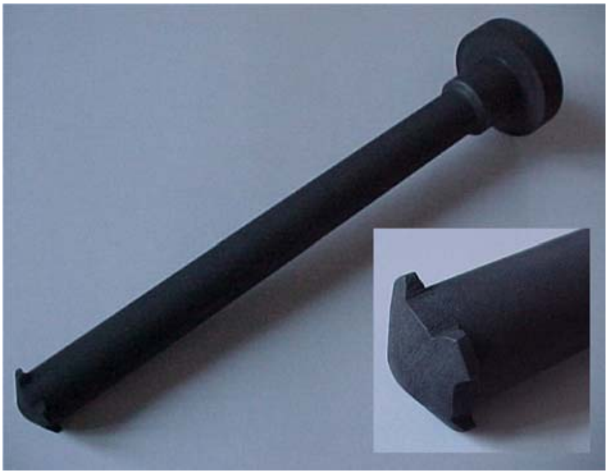

Fig. 1 Photograph of the thermometer well of the *Co_4N8_long* cell with an enlargement of the bottom, specially designed to allow a safe vertical introduction into the crucible

2.2 Furnaces

The Cu point was realized in the furnace described in [4], consisting basically of an Inconel comparator block heated by a system made of three different and partially overlapped electrical heaters.

Two different commercial furnaces were used to realize the Co–C point. A vertical single-zone furnace equipped with six heating elements made from silicon carbide for operation up to 1,600 °C was used with the *Co_4N8_big* cell. The furnace can be operated both horizontally and vertically, depending on the specific application. The heated chamber is 450 mm in length, and a zone uniform in temperature to within ±5 °C is assured over a length of 350 mm. An Al_2O_3 tube, 43 mm in diameter, was used to accommodate the crucibles.

A vertical high-temperature furnace was used both for filling the *Co_4N8_long* cell and, thereafter, for the measurements with Pt/Pd thermocouples. It is a single–zone furnace equipped with molybdenum disilicide ($MoSi_2$) heaters for operation up to 1,800 °C. The heating elements are installed in a hanging position inside a rectangular housing made of high-grade insulation materials and surround the one-end-closed alumina tube containing the fixed-point cell. The heated chamber is 500 mm in length and an Al_2O_3 tube, 43 mm in diameter, was used to accommodate the crucibles.

2.3 Measurements and Results

The measurements at the fixed points of Ag, Al, Zn, Sn, In and at the triple point of water are described in [3]. During the present exercise, the five Pt/Pd thermocouples were calibrated at the eutectic point of Co–C and thermocouples ET, Ea, and I1 also at the freezing point of Cu.

2.3.1 Measurements with Co–C Cells

A single melt–freeze run was performed for each thermocouple calibrated with the *Co_4N8_big* cell, and three runs were made with the *Co_4N8_long*. Figure 2 shows two typical melt curves obtained using thermocouple Ea+ in the *Co_4N8_big* and *Co_4N8_long* cells. The figure clearly shows a higher melting temperature for the *Co_4N8_long* cell, a result which will be discussed later. Shorter plateaux were obtained with the longer cell, probably as a consequence of the reduced ingot shell surrounding the thermometer well.

To assign the emf value corresponding to the transition temperature of the melting curve, it is common practice in the thermometry community to take the first derivative of the melting process with respect to time, as summarized in the review paper in [7]. Similarly, a melting histogram can be drawn and the temperature (or the thermocouple emf) corresponding to its maximum taken. In this procedure, the melting temperature is identified with the average emf of the flattest part of the plateau. Emf steps of 0.5 μV were adopted to generate the histogram. Figure 3a and b shows the histogram and the first derivative of a typical melting curve.

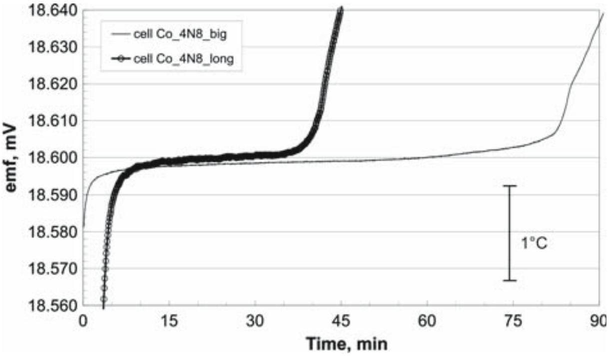

Fig. 2 Typical melt curves obtained with the two Co–C cells

The repeatability of the melting process was good with the determinations for each thermocouple always within ±0.5 µV.

A systematic difference—the emf measured with the longer cell was higher than that with the shorter one—was found in the calibrations performed with the two Co–C cells with all thermocouples except I2. An average difference of 1.0 µV (std. dev. of 0.25 µV) was found. For thermocouple I2, no significant difference was found in the emfs generated with the two cells.

The results obtained with the two cells and with different furnaces are extremely encouraging. The difference of 1.0 µV, even if systematic, is very limited in extent and could be due to the increased immersion of cell *Co_4N8_long* or to different environmental conditions specific to the two furnaces. Insensitivity to the thermal environment was also found in [8] where largely different furnaces were used.

2.3.2 Measurement Uncertainty

A combined expanded uncertainty between 0.05 °C and 0.1 °C ($k = 2$) was estimated for calibration up to the Ag point [3]. The inclusion of the Co–C point requires further considerations.

Inhomogeneity, which can be one of the larger components of the uncertainty budget, was assessed at the Ag point and in a potassium gas-controlled heat pipe at 930 °C and reported in [3]. For all thermocouples but ET, the emf variations were within the equivalent of less than 0.05 °C when immersion profiles were measured over a length of 12 cm. Half of this change, i.e, 0.025 °C, may be taken as the uncertainty contribution from inhomogeneity. The inhomogeneity measured at the Ag point (or at 930 °C), when expressed as a percentage of the total emf, is representative of the inhomogeneity at other temperatures [9]. Therefore, the inhomogeneity uncertainty contribution calculated for the Co–C point is 0.035 °C.

Other uncertainty contributions include reproducibility of the melting plateau, analysis of the melting curves, emf measurements, and properties of the cell. A combined uncertainty of 0.08 °C ($k = 1$) is estimated for the calibration of the thermocouples at the Co–C point.

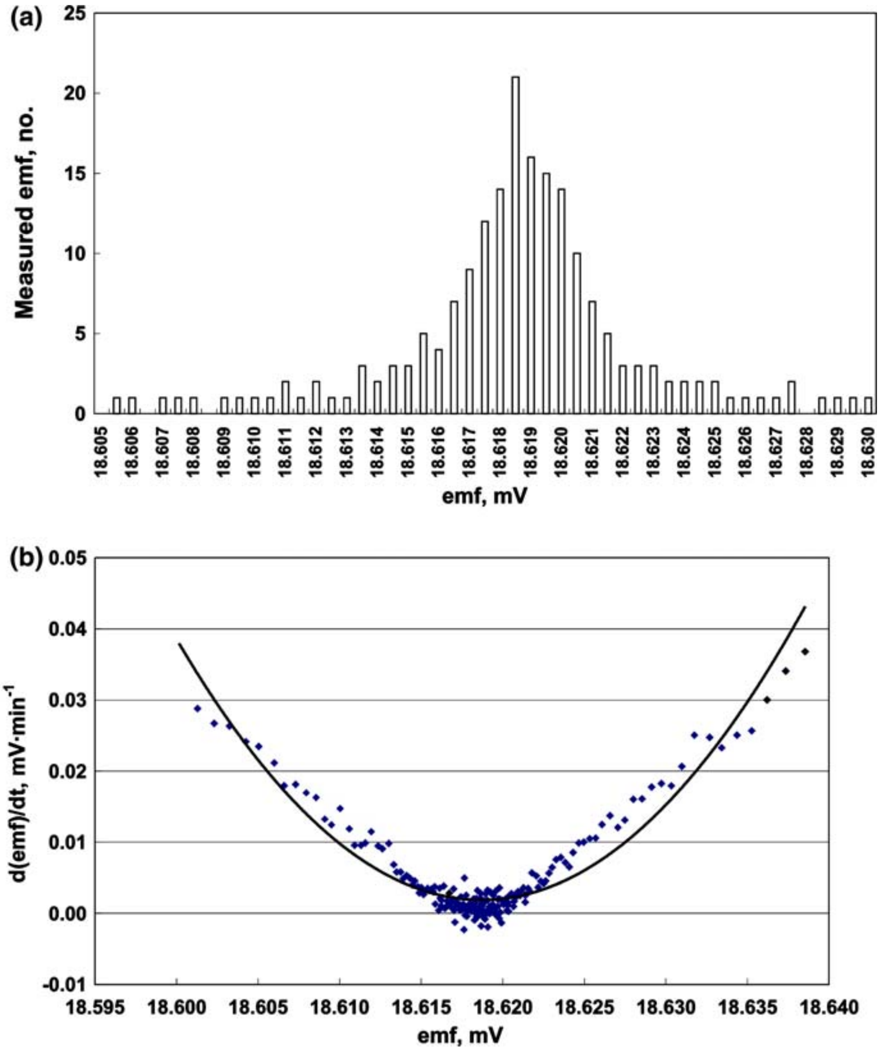

Fig. 3 (**a**) Melting histogram and (**b**) plot of the first derivative with respect to time of a typical melting curve

2.3.3 Discussion of the Results

As a first indication of the results, the deviations of the measured emf values at the fixed points from the reference function (now included in the IEC 62640 standard) were calculated for each thermocouple. For the purpose of calculation, a value of 1,324.0 °C was assumed for the Co–C transition point, as proposed in [10], and supported by the CCT-WG5 for the inclusion of the Co–C eutectic as a secondary reference point for the approximation of the ITS-90.

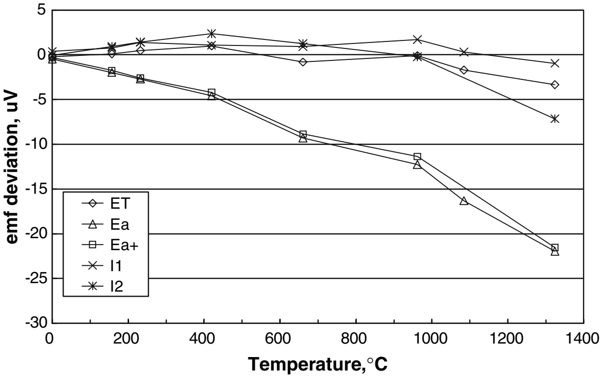

Fig. 4 Emf differences with respect to the Pt/Pd reference function measured with the five INRIM thermocouples at the different fixed points

Table 2 The rms residuals of the deviations of the measured emf values with respect to the reference function

Thermocouple	rms Residuals, in equivalent °C	
	Calibration up to the Co–C point	Calibration up to the Ag point
ET	0.038	0.046
Ea	0.042	0.046
Ea+	0.053	0.048
I1	0.030	0.037
I2	0.031	0.023

Figure 4 shows the differences for all five thermocouples. For each thermocouple, the deviations were fitted with a second-order polynomial equation. Table 2 reports the rms residuals of the deviations of the measured emf values from the reference function compared with the rms residuals of the original calibration up to the Ag point for the five thermocouples. The analysis of the rms residuals shows an improvement of the fit for thermocouples ET, Ea, and I1 and a worsening for Ea+ and I2. Such a result tends to exclude possible systematic errors in the calibration at Cu and Co–C points.

The results of the calibration at the Co–C point were then analyzed by comparing them to the calibration with the radiation thermometer. The deviations of the emf values measured at the Co–C point were compared with the fitted deviation curves for the different thermocouples. A graphical presentation is shown in Fig. 5. Table 3 reports the differences, expressed in terms of temperature, between fixed-point and radiation thermometer calibrations. An average difference of −0.10 °C (std. dev. of 0.09 °C) is calculated and all individual results are well within the combined standard uncertainty, which is estimated to be 0.43 °C, a figure obtained by combining in quadrature the uncertainty in the radiation thermometer calibration, 0.30 °C [2], the uncertainty in the Co–C temperature, 0.30 °C [10], and the uncertainty in the fixed-point calibration, 0.08 °C. The agreement is particularly significant and confirms the validity, within the respective estimated uncertainties, of:

(i) the reference function for Pt/Pd thermocouples;
(ii) the temperature assigned to the Co–C point;

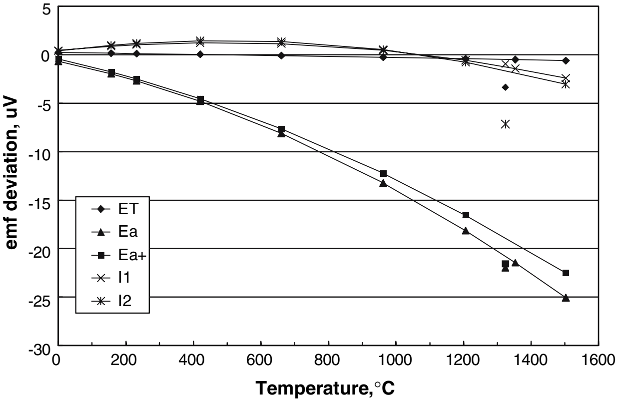

Fig. 5 Comparison of the emf deviations measured at the Co–C point (symbols positioned at 1,324 °C) and those obtained with the radiation thermometer calibration (deviation curves)

Table 3 Differences in terms of temperature between the calibration at the Co–C point and the calibration by comparison with the radiation thermometer

Thermocouple	ΔT (°C)
ET	−0.12
Ea	−0.05
Ea+	−0.12
I1	0.01
I2	−0.24

A value of 1324.0°C was assumed for the Co–C point

(iii) the calibration of Pt/Pd thermocouples by comparison with the standard radiation thermometer at INRIM; and
(iv) the realization of the Co–C point at INRIM.

However, as the average difference is the result of systematic deviations measured with all the thermocouples, an error could be associated with one of the previous points. Further investigations will be aimed at disclosing such errors.

3 Summary

Two Co–C eutectic fixed-point cells were used to extend a calibration procedure to calibrate Pt/Pd thermocouples based entirely on fixed points. The Co–C point is one of the most interesting metal-carbon eutectic points because of its possible applications in contact and radiation thermometry and its economy stemming from the relatively low cost of the materials required, which makes it particularly attractive as a transfer standard for temperature scale dissemination.

The Co–C eutectic point proved to be particularly useful because of its good reproducibility, as indicated by its relative insensitivity to the thermal environment. In fact, cells of different design used with different furnaces produced results in agreement within a few hundredths of a degree. Five Pt/Pd thermocouples made with wires of different purities and from different manufacturers were calibrated at fixed points from the triple point of water to the Co–C point, and the inclusion of the latter did not significantly modify the quality of the calibration.

The results were also compared to those obtained in a previous calibration with the standard radiation thermometer. The differences were within 0.24 °C for all five thermocouples with an average difference of 0.10 °C, a result well within the combined standard uncertainty of 0.43 °C.

The addition of the Pd-C eutectic point (1,492 °C) will allow Pt/Pd thermocouples to be calibrated over their entire range of operation, namely from 0 to 1,500 °C, by means of fixed points. Such an approach will simplify the calibration by avoiding the troublesome procedure based on comparison with a standard radiation thermometer through a blackbody transfer source.

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