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Investigation of the Behavior of the Co–C Eutectic Fixed Point

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Abstract The behavior of the Co–C eutectic fixed point was investigated at INRIM. Several cells of different design and volume, and filled with cobalt of different purity were constructed and investigated with both Pt/Pd thermocouples and radiation thermometers. The melting behavior was investigated with respect to the melting rate, the pre-freezing rate, and the annealing time. The melting temperatures, as defined, were not significantly affected by the different testing conditions, even if the shape and duration of the plateaux were influenced. Several tens of melt and freeze cycles were performed with the different cells. The spread in the results for all of the different conditions was very limited in extent, giving rise to a standard deviation of less than 0.04 °C; a repeatability of better than 0.02 °C was found with both Pt/Pd thermocouples and radiation thermometers. The results of our measurements are encouraging and confirm the suitability of Co–C as a reference point for the high-temperature range in a possible future temperature scale. Investigations of long-term stability remain ongoing.

Keywords Co–C · Eutectics · Fixed points · Metal–carbon · Radiation thermometry

1 Introduction

The Co–C eutectic is an interesting new high-temperature fixed point. Unlike most of the other metal (carbide)–carbon eutectics, it is not too expensive to realize, and thus, it is a good candidate for studies, as it allows more cells to be produced and investigated with respect to the different effects that might influence the metrological behavior.

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Furthermore, its economy makes it suitable for widespread diffusion among a large number of laboratories. The range of applications is wide, as the Co–C fixed point may be used in contact thermometry for the calibration of Pt/Pd thermocouples [1–3], and in radiation thermometry both as a reference point for a scale realization or as a further point to extend the operating limits of the "fixed-point calibration technique" in IR thermometry [4]. Co–C has been proposed [5] and supported by the CCT-WG5 on radiation thermometry as a secondary reference point for the approximation of the ITS-90 or as a point underpinning a 'mise en pratique' for thermodynamic temperature.

Since there are a large number of metal (carbide)–carbon fixed points, many metrological investigations still need to be carried out despite the numerous articles that have been published during the intervening 8 years since they were first proposed by Yamada et al. [6]. One of the most critical phenomena is the possible dependence of the transition temperature on the pre-freezing conditions and annealing time, as was demonstrated by Sasajima et al. [7] for Fe–C. This phenomenon is a well-known aspect of the metal–metal eutectics (for example, Cu–Ag [8]) that compromised, in past years, their use as precision fixed points. It is consequently important to understand if such behavior is specific to the Fe–C eutectic or if it also affects other metal (carbide)–carbon fixed points.

At INRIM, several cells of different design and volume (10 cm^3 and 43 cm^3), and filled with Co of different purity (99.9% and 99.998%) were constructed and investigated with both Pt/Pd thermocouples and radiation thermometers. The article will describe the different cells, the experimental arrangement, and the measurements carried out with both contact and radiation thermometers.

2 CO–C Fixed-point Cells

Different fixed-point cells were prepared and investigated. A common general design of the cell was selected with the following principal dimensions: outer diameter—42 mm; length—110 mm; inner volume—43 cm^3; blackbody aperture diameter—8.5 mm; and length of the cavity—88 mm. All crucible components were made from high-purity graphite with less than 10 ppm ash content. The crucibles were designed in such a way that they could be used both for contact thermometry and radiation thermometry; the 8.5 mm diameter cavity can be used both as a blackbody cavity for a radiation thermometer observation and as a thermometer well for thermocouple insertion. It is also worth mentioning that such an approach enables the contact thermometry measurements to be directly traceable to T_{90}.

The first cell was filled with 99.9% pure cobalt powder supplied by Goodfellow. Graphite powder, 99.9999% pure, supplied by Alfa Aesar was used to prepare the cobalt–carbon mixture for all the fixed points. The first cell will be identified as *Co_3N_big*.

Another cell of the same design was then filled with cobalt of 99.998% purity from Alfa Aesar (cell identified as *Co_4N8_big*). A smaller crucible was obtained by inserting a graphite sleeve and an additional graphite disc to reduce the effective inner volume to about 10 cm^3, and it was then filled with the 99.998% pure cobalt (cell *Co_4N8_small*). Schematics of the cells are shown in Fig. 1; drawing (a) refers to the "big cell," whereas drawing (b) shows the "small cell."

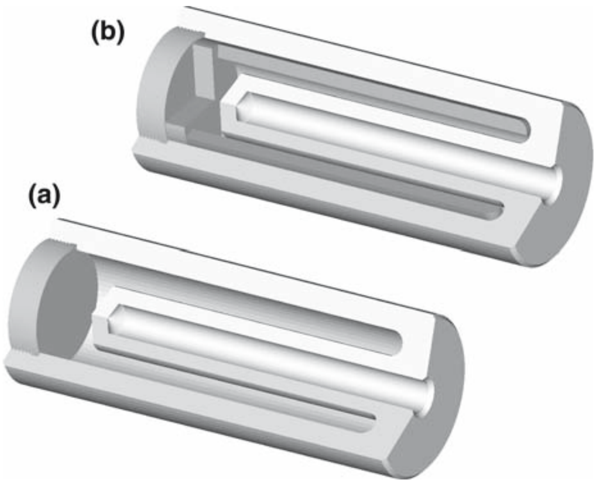

Fig. 1 Diagrams of the Co–C fixed point cells: (**a**) cell in its original design and (**b**) “small cell” with the addition of graphite sleeve and disc

Powder mixtures of approximately the eutectic composition were prepared to fill the crucibles. More than 10 repeated fillings were necessary to completely fill the individual cells (16 fillings were necessary for the *Co_4N8_big* cell). At each filling, the crucibles were heated for about 1 h at (15–20) K above the eutectic melting temperature, and then slowly cooled to room temperature.

3 Experimental Context

3.1 General Aspects

Investigations were mainly conducted through contact thermometry experiments supplemented by additional measurements with a radiation thermometer. This was because some effects can be better investigated by contact thermometry, provided that suitable sensors are used. A contact measurement is free from certain uncertainty components that may dominate measurements by radiation thermometry, like the size-of-source effect, with a consequent improvement in accuracy. A selected Pt/Pd thermocouple possesses the required homogeneity, repeatability, and high-temperature stability to be conveniently used. A possible source of uncertainty in contact measurements could be heat-leakage (conduction) effects due to the limited immersion depth of the cells. Experiments carried out with a longer cell specifically designed for contact thermometry applications (135 mm immersion depth [3]) indicated substantial agreement with the other cells.

3.2 Equipment

A single-zone furnace equipped with six heating elements made from silicon carbide for operation up to 1, 600 °C was used for the present investigations. The furnace could be operated both horizontally and vertically. The heated chamber was 450 mm in length, and a zone uniform within 5 °C was assured over a length of 350 mm. An Al_2O_3 tube, 43 mm in diameter, was used to accommodate the crucibles.

For the measurements with the Pt/Pd thermocouple, the furnace was positioned vertically and the thermocouple, identified as I1, was inserted into the fixed point. Thermocouple I1 is one of the thermocouples investigated at INRIM that closely matches the reference function and exhibits excellent homogeneity, high temperature stability, and calibration accuracy [3,9].

Measurements with a radiation thermometer, with the furnace in the vertical position, were carried out with the improved version [10] of the precision transfer standard developed for the EC-funded project TRIRAT ("TRaceability in Infrared RAdiation Thermometry") and used in the European comparison of local realization of temperature scales. The instrument, originally designed for the realization of temperature scales from the In (156.5985 °C) to Cu (1, 084.62 °C) points, was further modified for the present experiment, and its electronics were adapted for the increased input signal dynamic range. The thermometer, based on an InGaAs photodetector with a 5 mm diameter sensing area (Hamamatsu Model G5832-15) and cooled to −10 °C by means of a thermoelectric cooler, works in a narrow spectral band centered near 1.6 μm. Its main features, namely its low size-of-source effect, high temperature resolution, and both short- and long-term stability, made it particularly suitable for the present investigation.

4 Measurements

4.1 Introduction

Repeated melt-freeze runs were performed with the three cells. All the cells were investigated with the Pt/Pd thermocouple (37 complete runs with *Co_3N_big*; 30 runs with *Co_4N8_small*, and 15 runs with *Co_4N8_big*). Only the *Co_4N8_small* cell was used with the radiation thermometer (15 runs). Complete melt-freeze runs were performed, but only melting curves were analyzed because of the agreed recognition among experimenters that melts are more reproducible than freezes.

To assign a temperature value (or an emf value, or a radiation thermometer signal) to a melting curve, it is common practice in the international thermometry community to take the first derivative of the melting process with respect to time [11]. Similarly, a melting histogram can be drawn and the temperature (or emf, or radiation thermometer signal) corresponding to its maximum taken. Figure 2a and b shows the histogram and the first derivative of a typical melting curve, and illustrate the equivalence of the two methods.

4.2 Repeatability; *Co_4N8_small* cell

4.2.1 Thermocouple Measurements

The *Co_4N8_small* cell was preliminarily tested and some repeatability checks were carried out with the aim of deriving useful information to help discern the significance

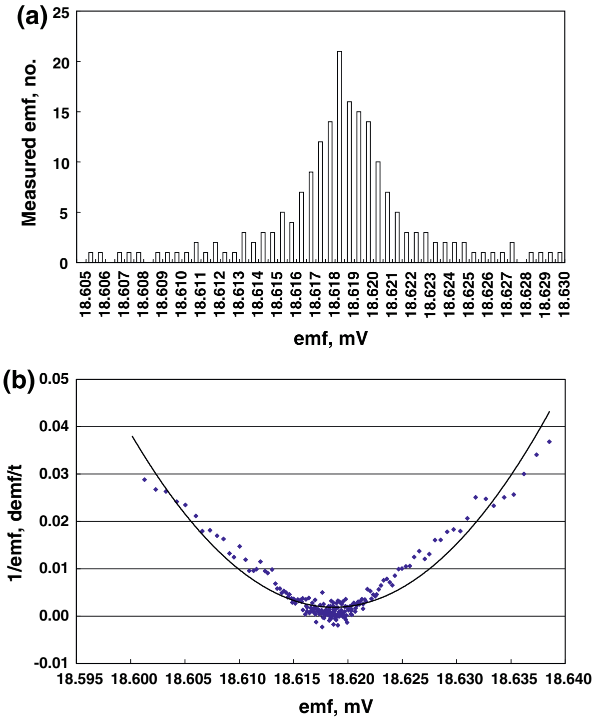

Fig. 2 (**a**) Melting histogram and (**b**) plot of the first derivative with respect to time of a typical melting curve

of the results of the later investigations. Seven melts were induced by offsetting the furnace 7 K with respect to the eutectic temperature following freezes induced with an offset of −2.5 K (see Fig. 3). The resulting melting emf values were within 0.5 μV (corresponding to 0.02 °C) and had a standard deviation of less than 0.2 μV (i.e., less than 0.01 °C).

4.2.2 Non-contact Measurements

The *Co_4N8_small* cell was also investigated with the radiation thermometer, and 15 runs were performed. Melts were induced by setting the furnace 5 K above the eutectic temperature following freezes induced with a −5 K furnace offset. Because all runs were performed with the same conditions, the results are representative of the repeatability of the process. A signal standard deviation corresponding to about 0.017 °C was found, which is similar to that found for the measurements with the Pt/Pd thermocouple. It is an interesting result, which suggests that the variation may be attributed to the fixed-point itself without significant contributions from the measurement processes, which are certainly different for the thermocouple and radiation thermometer measurements.

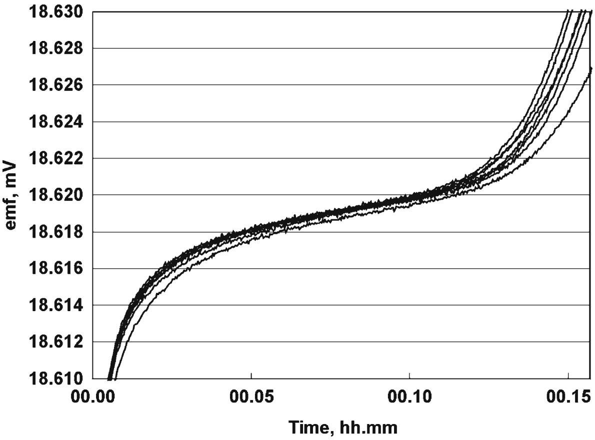

Fig. 3 Results of repeatability tests (melts induced by an offset of 7 K with respect to the eutectic temperature following freezes induced by an offset of −2.5 K)

4.3 Effect of the Melting Rate; Thermocouples; *Co_4N8_small* cell

Figure 4a and b shows different melting curves obtained with the *Co_4N8_small* cell. Figure 4a shows three melting curves obtained with different offsets of the furnace temperature setting (+2, +5, and +10 K with respect to the melting temperature) following a freeze induced with an offset of −2 K. In Fig. 4b, similar curves are presented for melts following freezes induced with an offset of −5 K. The melting temperatures for a −2 K offset are within 0.02 °C with an average thermocouple signal of 18.620_{25} mV. A slightly higher spread (0.03 °C) was found for the −5 K setting, but with exactly the same average emf (18.620_{25} mV). Taking into account the repeatability of the melting curves discussed in the previous subsection, the present results indicate that the melting temperatures are practically unaffected by the melting rate, even if the melting range increases with increasing furnace offset.

4.4 Effect of the Pre-freezing Rate and Annealing Time; Thermocouples; *Co_4N8_small* cell

Results shown in Fig. 4a and 4b shows that different furnace offsets for the preceding freeze, i.e., −2 K and −5 K, do not influence the melting temperatures. This effect was investigated in more detail and different plateaux were obtained at the same melting rate (furnace offset by +9 K), but with different rates for the preceding freeze. The furnace was kept for 180 min, starting from the initiation of the freeze, at temperatures from −2 K to −20 K below the freezing temperature. The results are shown in Fig. 5. The four melting plateaux produced an average melting emf of 18.619_9 mV, with the range of values within 0.75 μV—corresponding to 0.03 °C. These results are comforting, and allow us to say that the significant dependence of the melting temperature on the pre-freezing rate reported for Fe–C [7] is not a general behavior of metal–carbon eutectics and that, in any case, the Co–C point is free of such dependence.

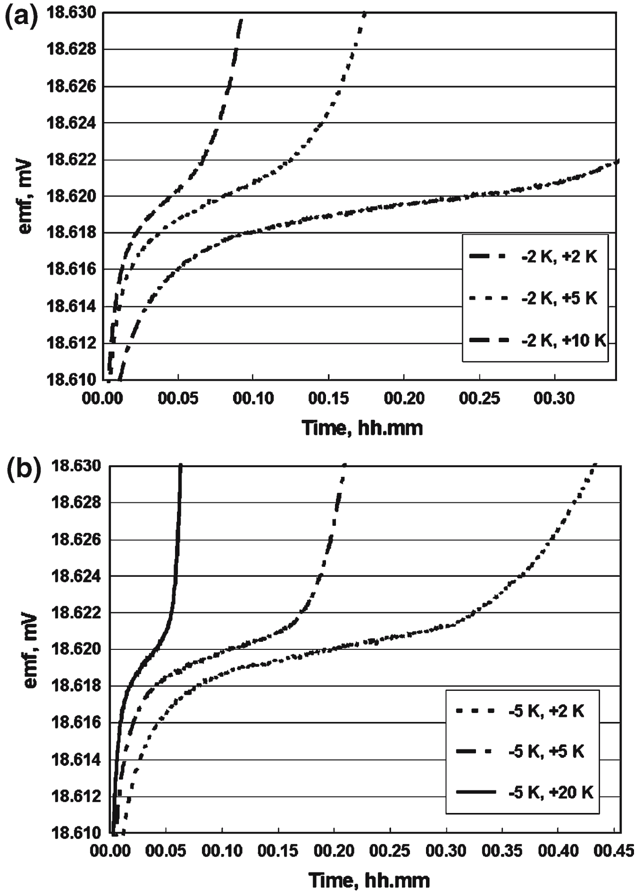

Fig. 4 Effect of melting rate on the melting curve for different preceding freezes induced by different furnace temperature offsets: (**a**) −2 K and (**b**) −5 K

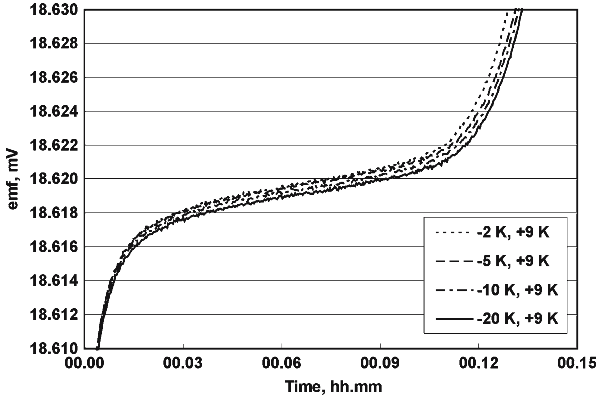

Fig. 5 Effect of preceding freezing rate on the melting curve

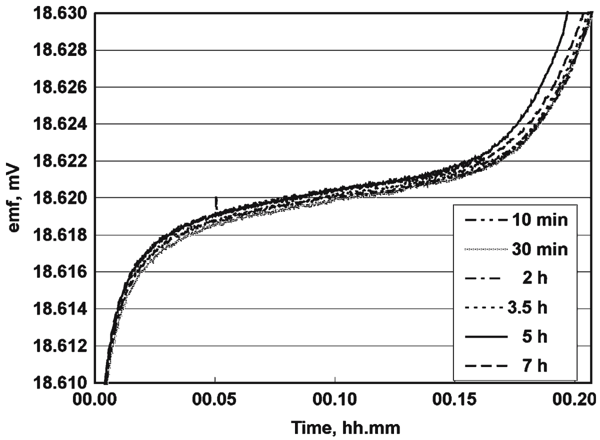

Fig. 6 Effect of the annealing time on the melting curve following a −5 K offset to induce the freeze

Table 1 Summary of repeatability checks, melting rate, pre-freezing rate, and annealing time tests with the *Co_4N8_small* cell

	Contact measurements				Non-contact measurements
	Repeatability	Melting rate	Pre-freezing rate	Annealing time	Repeatability
Average emf (mV)	18.619_5	18.620_{25}	18.619_9	18.620_{75}	–
Min–max (°C)[a]	0.02	0.03	0.03	0.02	0.06
SD (°C)	0.01	0.014	0.016	0.01	0.017

[a] Temperature range encompassing all the determinations

Investigations in [7] also showed dependence of the melting behavior of the Fe–C eutectic on the annealing time in the solid state, prior to melting. The *Co_4N8_small* cell was kept −5 K below the freezing temperature for annealing times between 10 min and 7 h. The results are shown in Fig. 6. The average emf value was 18.620_{75} mV, with a standard deviation of 0.22 μV (0.01 °C). For Co–C, no significant dependence on annealing time was found.

A summary of the repeatability checks, melting rate, pre-freezing rate, and annealing time tests with the *Co_4N8_small* cell is given in Table 1. It is worth mentioning that all 23 melts described for the *Co_4N8_small* cell produced an average emf of 18.620_1 mV with a standard deviation of 0.50 μV (0.021 °C).

4.5 Other Thermocouple Measurements

The same investigations, though less extensive, were performed with the *Co_4N8_big* cell. The results, similar to those for the *Co_4N8_small* cell, are summarized in Table 2.

Table 2 Summary of measurements with three Co–C cells

	Cell/thermometer			
	Co_3N_big/Pt/Pd	*Co_4N8_small*/Pt/Pd	*Co_4N8_big*/Pt/Pd	*Co_4N8_small*/ rad. thermometer
No. melts	37	30	15	15
Average emf (mV)	18.6083	18.6202	18.6195	–
Min–max (°C)[a]	0.30	0.075	0.06	0.06
SD (°C)	0.093	0.021	0.016	0.017

[a] Temperature range encompassing all the determinations

Measurements with the *Co_3N_big* cell did not follow the systematic variation of conditions as described above for *Co_4N8_small* and *Co_4N8_big*, but, in consideration of its low purity, different conditions were "randomly" tried, as it was only intended as a test cell. Consequently, individual results for this cell are not reported, though a summary will be given.

5 Discussion and Conclusion

Table 2 summarizes the results obtained with the three cells for both the Pt/Pd thermocouple and the radiation thermometer measurements. As anticipated, the results for cell *Co_3N_big* are shown, but they are not comparable to those obtained with the cells filled with the 4N8 pure cobalt. The temperature equivalent of the average thermocouple signal was found to be about 0.5 °C lower than the values obtained with the 4N8 cells (Lowe and Machin [12] found a depression of the melting temperature of 0.13 °C for a similar nominal purity, but the type and concentrations of the various impurities is extremely important at such a high impurity content and, in our case, a detailed analysis was unavailable). The spread of the results was significantly higher (standard deviation of 0.093 °C) compared to the results for the purer cells (0.02 °C).

The two cells of different volume, 43 cm^3 and 10 cm^3, filled with 4N8 pure cobalt were used to investigate the possible dependence of the transition temperature on the melting and pre-freezing rates and annealing time. The results are comforting because no significant difference was found in the repeatability. Further interesting results stem from the comparison of the two cells: the average signals agreed within 0.03 °C and the respective standard deviations were very close (0.021 °C and 0.016 °C). This difference is of similar magnitude as the repeatability and, consequently, indicates equivalence of the two cells, thus excluding any dependence on the volume of the cells.

The standard deviation of all 45 melts performed with both 4N8 cells is slightly higher, i.e., 0.023 °C, and the range in temperature encompassing all the results is 0.11 °C.

The results of the present investigation allow an important conclusion to be drawn: the dependence of melting temperature on the operational conditions during the melt-freeze cycles, found in [7] for the Fe–C point, is not a general characteristic of metal–

carbon eutectics, as demonstrated by the results obtained for Co–C. The numerical results, in terms of repeatability and reproducibility with respect to the tested operational conditions, confirm the suitability of the Co–C point as both for a defining point of a future scale and, thanks to its comparatively low materials cost, for dissemination.

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