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Cobalt-Carbon Eutectic Fixed Point for Contact Thermometry

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Abstract

Two Co-C eutectic fixed points were constructed for thermocouple calibration. The eutectic fixed points were measured with a Pt/Pd thermocouple calibrated at the freezing temperatures of Sn, Zn, Al, Ag, and Au. A temperature of 1323.99 °C ± 0.52 °C (k = 2) was determined via this method. The cell design allowed filling to be accomplished in a single step. Each cell was held above 1300 °C for at least 42 hours and was subjected to at least 20 melt/freeze cycles with no mechanical failure occurring.

Keywords: Co-C; Eutectics; High Temperature Fixed Points; Pt/Pd Thermocouples

1 Introduction

The melting temperature of the cobalt-carbon eutectic is ideally situated as a reference point for the calibration of high-temperature thermocouples above the melting point of silver. Since metal-carbon eutectic materials were first suggested as potential high-temperature fixed points by Yamada *et al.* [1] in 1999, a great deal of research has taken place internationally [2]. Cobalt-carbon eutectic fixed points are already being utilized to reduce the uncertainties in the calibration of thermocouples used in the heat treatment of turbine blades for the aerospace industry [3, 4].

A number of studies have been carried out to investigate the use of eutectics for thermocouple calibration [3, 4, 5-12]. Edler *et al.* [6] used four Pt/Pd thermocouples calibrated at two national measurement institutes (NMIs) (PTB and Inmetro) to obtain 1323.81 °C ± 0.27 °C (k = 2) for the melting temperature of Co-C. Sadli *et al.* [13] compiled temperatures from many radiation thermometry studies and suggested a temperature of 1324.0 °C ± 0.6 °C (k = 2) for Co-C.

The influence of the structure of eutectic materials on the eutectic melting temperature has been investigated by Lowe *et al.* [14] using optical microscopy and electron backscatter diffraction. The authors found a difference of 50 mK between the inflection points when the fixed point was frozen with the furnace 30 K below the transition temperature compared to the value when the fixed point was frozen with the furnace only 1 K below the transition temperature. The optical microscopy revealed a difference in the grain size of the frozen Co-C eutectic material. The difference in the microstructure is thought to result from differences in the rate at which the materials solidified from the melt. The influence of solidification rate on the melting temperature has also been investigated by Yang *et al.* [15]. Here, the authors found very little difference in melting temperature for furnace offsets up to 78 K below the melting temperature of Co-C.

Various crucible designs have been tested, some of which use graphite and/or C/C-composite liners to isolate the eutectic material from the crucible to provide a sacrificial layer to accommodate the expansion of the eutectic, and provide better thermal uniformity over the length of the ingot [16, 17]. Recent long-term stability studies have shown that (for the Co-C eutectic) the C/C sheet may eventually dissolve in the eutectic material and cause the crucible to fail [18, 19]. Most of the designs currently in use require multiple filling steps before the crucible is suitably full.

In this work, a unique crucible design and a custom-built vertical, single-zone furnace using molybdenum disilicide heating elements are used to cast and evaluate two Co-C eutectic fixed points. A Pt/Pd thermocouple calibrated at the Sn, Zn, Al, Ag and Au fixed points of the ITS-90 is used to measure the melting temperature.

2 Experimental Methods

2.1 Single-Zone Furnace

A single-zone furnace (built in-house) having four u-shaped molybdenum disilicide heating elements was used as both the casting and measuring furnace. A description of the furnace is given elsewhere in these proceedings [20]. An alumina protection tube (42 mm diameter, 711 mm long, and dedicated to Co-C eutectics) containing the Co-C fixed point under study was placed within the main furnace tube. A stainless-steel, water-cooled cap was attached and sealed to this tube by way of a Teflon ring. The cap's central hole allowed the thermocouple protection tube to be inserted and sealed via an o-ring. The cap also contained inlet and outlet connections for evacuation and inert gas flow. The sealed protection tube containing the fixed point was evacuated and flushed with Ar twice prior to each heating cycle. A slow Ar flow was maintained during measurement. The alumina protection tube (6.5 mm diameter, 711 mm long, 99.7 % pure) containing the Pt/Pd thermocouple was baked in air at 1100 °C for 15.5 hours prior to its first use. This protection tube was used only with the Co-C fixed points.

2.2 Fixed Point Construction

Four Co-C fixed-point cells were created using the design shown in Figure 1. The high-purity graphite (2020-P) crucibles obtained from Carbone of America (Bay City, MI) were constructed from material with less than 20 ppm ash content. When assembled, the fixed-point cells are 170 mm in height and 33 mm in diameter. The thermocouple well is 148 mm deep and 7 mm in diameter. The two additional holes around the thermometer well at the top of the crucible were included in the design to accommodate additional thermocouples; however they are not normally used. The tapered design of the outer and inner pieces produced an internal volume (for the eutectic material) that was calculated to be ~ 14 cm^3. Figure 2 is an x-ray image of the cell CoC-2 that was filled in a single casting step. The height of the ingot is approximately 85 mm.

The first fixed point (CoC-1) was found to give melting and freezing curves with much greater slope than the 2nd (CoC-2) and 3rd (CoC-3) fixed points. This was attributed to the thermowell not being fully inserted into the ingot on casting. The fourth fixed point cell (CoC-4) was cast using only 50% of the starting materials (compared to CoC-2 and CoC-3) to explore the effect of a shorter ingot. However, the melting and freezing curves of CoC-4 were found to be much shorter and have greater slope than those of CoC-2 and CoC-3. This is most likely due to a combination of insufficient immersion of the thermocouple in the ingot and greater coupling of the thermocouple to the furnace. All the data presented here pertain to CoC-2 and CoC-3.

The starting materials for the eutectic fixed points were the same: 99.995% pure Co slugs and 99.9999% pure graphite – both obtained from Alfa Aesar. The purity of the Co was confirmed by glow-discharge mass spectrometry performed at the National Research Council Canada's Chemical Metrology facility. The starting materials were mixed at approximately the eutectic composition of 2.6 wt.% C. Each crucible was charged with nominally 92 g of starting material (Co + C). Casting was performed by slowly evacuating the alumina protection tube containing the crucible and starting materials and flushing with argon 3 times. The furnace temperature was then raised to 300 °C and the tube evacuated and flushed once more. The furnace temperature was then raised (at a rate of 0.15 $K \cdot s^{-1}$) to 20 K or 18 K above the Co-C melting temperature for CoC-2 and CoC-3, respectively. The fixed points were filled in a single step and the thermowell of the crucible pushed into place using the thermocouple protection tube once the starting materials had alloyed and melted.

2.3 Pt/Pd Thermocouple Preparation

A Pt/Pd thermocouple (Pt/Pd-4) was prepared using 0.5 mm diameter, 99.99+% pure Pd wire obtained from Johnson Matthey (batch number NM35415) and 0.5 mm diameter, 99.998% (nominally) Pt wire obtained from Alfa Aesar. Each leg was cleaned by wiping with a commercial degreaser, acetone, ethyl alcohol and finally with distilled water. The individual wires were then electrically annealed at approximately 1300 °C for 8.5 hours and then at approximately 480 °C for 2 hours. The Pt and Pd wires were then inserted into twin-bore alumina sheaths (99.7%) which had been baked in air at 1100 °C for 15.5 hours. The Pt and Pd legs were then joined by welding a strain-relieving coil of 0.13 mm diameter, reference-grade Pt wire. The thermocouple was placed in an alumina protection tube that had been baked in air at 1100 °C for 15.5 hours. The assembled thermocouple was annealed in air first at 1100 °C for 3 hours then at 480 °C for a total of 24 hours by placing it in a horizontal tube furnace. The thermocouple was then calibrated at the freezing points of Sn, Zn, Al, Ag and Au. Pt/Pd-4 was used to measure the melting and freezing plateaus of Co-C (1324 °C) and Pd-C (1492 °C) and then recalibrated at the freezing points of Sn, Zn, Al, Ag and Au.

Figure 3 shows the results from the calibration of Pt/Pd-4. ΔEMF is the difference between the EMF measured by the thermocouple and the value given by the NIST-IMGC reference function [21] at the ITS-90 fixed point. A quadratic fit to the five calibration points gave a better goodness-of-fit (lower reduced-χ^2) than a linear fit. The quadratic fit provided a correction function that was extrapolated to the melting temperature of Co-C (1324 °C) where a correction of 7.23 μV was added to the measured EMF and the temperature estimated by using the corrected Pt/Pd-4 EMF in conjunction with the NIST-IMGC reference function.

2.4 Measurement Procedure

The furnace containing the fixed-point cell was heated at a rate of approximately 0.15 $K \cdot s^{-1}$ to a temperature 13 K below the Co-C melting temperature. The furnace was held at this temperature until the Pt/Pd thermocouple had equilibrated. The furnace temperature was then raised to approximately 5 K above the eutectic temperature. Once the melting plateau had completed and the Pt/Pd thermocouple had equilibrated with the furnace, the furnace was allowed to cool to a temperature 33 K to 5 K below the eutectic melting temperature. The varying furnace offset temperatures were used to investigate the effect of the freezing rate on the subsequent melting plateau temperature; however, no effect was noticed.

3 Results

Figure 4 shows selected melting plateaus measured for both CoC-2 and CoC-3 using Pt/Pd-4. These four plateaus represent the maximal variations in the inflection point observed during the measurements. The plateaus with the highest and lowest inflection points differed by 160 mK. The inflection point of all the melting curves was determined in three ways: a cubic polynomial was fit to the plateau and the minimum of the derivative was used; a numerical derivative was taken with the minimum determining the inflection point; the plateau data was sorted into bins of 0.17 μV, a histogram was plotted, and the peak of the histogram taken as the inflection point. Figure 5 shows the inflection point determined for each melting plateau measured. Each point represents the average of the three methods used to determine the inflection point for each melting plateau. The average of all the measurements of the Co-C fixed point was found to be 1323.99 °C. The standard deviation of the all the inflection points was 0.12 °C. It appears from Figure 5 that there may be some drift to higher temperature of either the cell melting temperature or the Pt/Pd thermocouple, although the magnitude of this drift is small compared to the uncertainty associated with the measurement.

Fixed point CoC-2 was subjected to 20 melt-freeze cycles (10 cycles from room temperature to the melting temperature) and was above 1300 °C for approximately 42 hours in total. Fixed point CoC-3 was subjected to 21 melt-freeze cycles (9 cycles from room temperature to the melting temperature) and was above 1300 °C for approximately 42 hours in total. Melting curves (normalized to their respective inflection points) for each fixed point cell are shown in Figure 6. There is some evidence of shortening of the plateaus over time, but the plateau shape does not appear to change significantly.

4 Measurement Uncertainty

The uncertainty was calculated by adding in quadrature the following components:

δE_{Cal}: uncertainty in the thermocouple calibration at the Sn, Zn, Al, Ag and Au fixed points;

δE_{Ex}: uncertainty in the extrapolation of the calibration to 1324 °C;

δE_0: uncertainty of the reference junction temperature;

δE_{El}: uncertainty of the electrical measurements;

δE_{Inf}: uncertainty in determining the inflection point;

δE_{TH}: thermocouple inhomogeneity;

δE_{Ref}: uncertainty in the thermocouple reference function;

δE_{Rep}: repeatability of the inflection point and;

δE_{HF}: uncertainty due to heat flux to the thermocouple.

Table 1 gives the values estimated for each component that contributes to the uncertainty. The uncertainty in the NIST-IMGC reference function was estimated to be 4.5 μV (0.178 °C) from Ref. [21]. The thermocouple inhomogeneity was assessed by evaluating the immersion profile over a distance of 135 mm in a Zn fixed point. The immersion profile in the Zn fixed point was obtained after the measurements of the Co-C fixed points. The inhomogeneity was found to be 0.019 % of the EMF and this relative value was assumed at all temperatures [22]. Zn was chosen as the fixed point to assess the inhomogeneity as it is the ITS-90 fixed point with the highest temperature that does not cause oxidation of the thermocouple [23]. The uncertainty in the extrapolation of the calibration to 1324 °C was estimated from the difference between a linear extrapolation and a quadratic extrapolation. This difference was estimated to be 2.5 μV which corresponds to 0.106 °C at 1324 °C. Figure 7 shows the temperature profile measured during a melting plateau of the CoC-2 fixed point. This temperature profile was used to estimate the uncertainty of the thermocouple measurement due to heat flux effects (2.7 μV). This value was determined by considering the variation in the measured EMF over a length of 50 mm from the bottom of the thermometer well while taking into account the change in the temperature over the length of the melting plateau. The uncertainty in determining the inflection point of the melting curves was estimated as the standard deviation of the three methods used to determine the inflection point for each melting curve (as described in Section 3). The repeatability was taken as the standard deviation of the inflection point of all the Co-C measurements using Pt/Pd-4.

5 Conclusions

Co-C eutectic fixed points have been produced and their melting temperature has been determined to be 1323.99 °C ± 0.52 °C ($k = 2$) by a Pt/Pd thermocouple calibrated at the fixed points of Sn, Zn, Al, Ag and Au. This value is in agreement with the value proposed by Sadli *et al*. [13]. The two cells have each been subjected to temperatures above 1300 °C for at least 42 hours and have not shown signs of mechanical failure. There may be some evidence of minor shortening of the length of the plateau over the > 20 melt/freeze cycles. Further studies are necessary to evaluate the long-term stability of the fixed points, but given the limited reduction in plateau length over ~ 20 cycles the crucible designs appears robust.

Acknowledgments

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Table 1 The sources and estimates of the uncertainty components.

Source	**Uncertainty at 1324 °C (K) (*k* = 1)**
Calibration at Sn, Zn, Al, Ag and Au, δE_{Cal}	0.062
Extrapolation of Calibration to 1324 °C, δE_{Ex}	0.106
Ice Point, δE_{0}	0.004
Voltage Measurement, δE_{El}	0.040
Determination of the Inflection Point, δE_{Inf}	0.010
Thermocouple Inhomogeneity, δE_{TH}	0.150
Thermocouple Reference Function, δE_{Ref}	0.110
Repeatability of the Inflection Point, δE_{Rep}	0.059
Heat Flux, δE_{HF}	0.114
Total	**0.26**

Figure Captions

Fig. 1 Schematic (left) and photograph (right) of the graphite crucible design used in this study.

Fig. 2 X-ray image taken of the fixed point CoC-2 after filling. The single filling step produced an ingot that was approximately 85 mm in height. It is not known what caused the uneven filling observed in the image although similar behaviour was observed in an x-ray image of a previous Co-C fixed point.

Fig. 3 Deviation from the reference function [21], (ΔEMF), of Pt/Pd 4 at the fixed points of Sn, Zn, Al, Ag and Au. The quadratic fit was used to extrapolate this deviation to the melting point of Co-C.

Fig. 4 Selected melting plateaus of the Co-C fixed points. The plateaus were chosen to represent the extremes of the measured inflection points. However, even the extreme inflection points differed by only 160 mK.

Fig. 5 The temperature of the melting point for all the measurements of CoC-2 (indicated by squares) and CoC-3 (indicated by circles) with Pt/Pd 4. Measurements 1 through 25 occurred sequentially. When a calibration or other measurement using Pt/Pd 4 was performed, it is indicated in the figure. The letters A through D above the points in the figure refer the curves labelled A through D in Figure 4.

Fig. 6 Plateau from each measurement day for a) CoC-2 and b) CoC-3 normalised to each plateau's inflection point for comparison of the plateau length over all the measurements. While some shortening of the plateaus is observed over time, the change is minimal compared to the length of the plateau. Further studies are needed to determine if the length of the plateau continues to shorten to a point where the fixed point becomes unusable or mechanically fails.

Fig. 7 Temperature profile measured during a melting plateau of the CoC-2 fixed point. This data was used to estimate the uncertainty in the thermocouple measurements due to heat flux. While the temperature did change over the duration of the melt plateau, measurements at the beginning and end of the temperature profile measurements allow for an estimate of the magnitude of this change.

Figures:

Figure 1:

Figure 2:

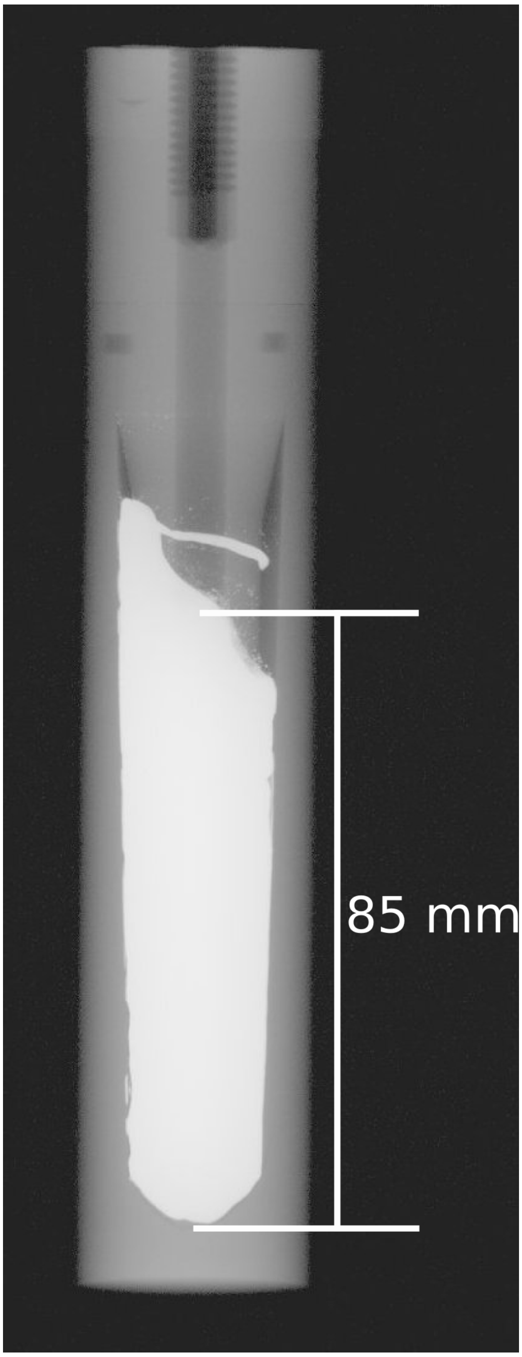


Figure 3:

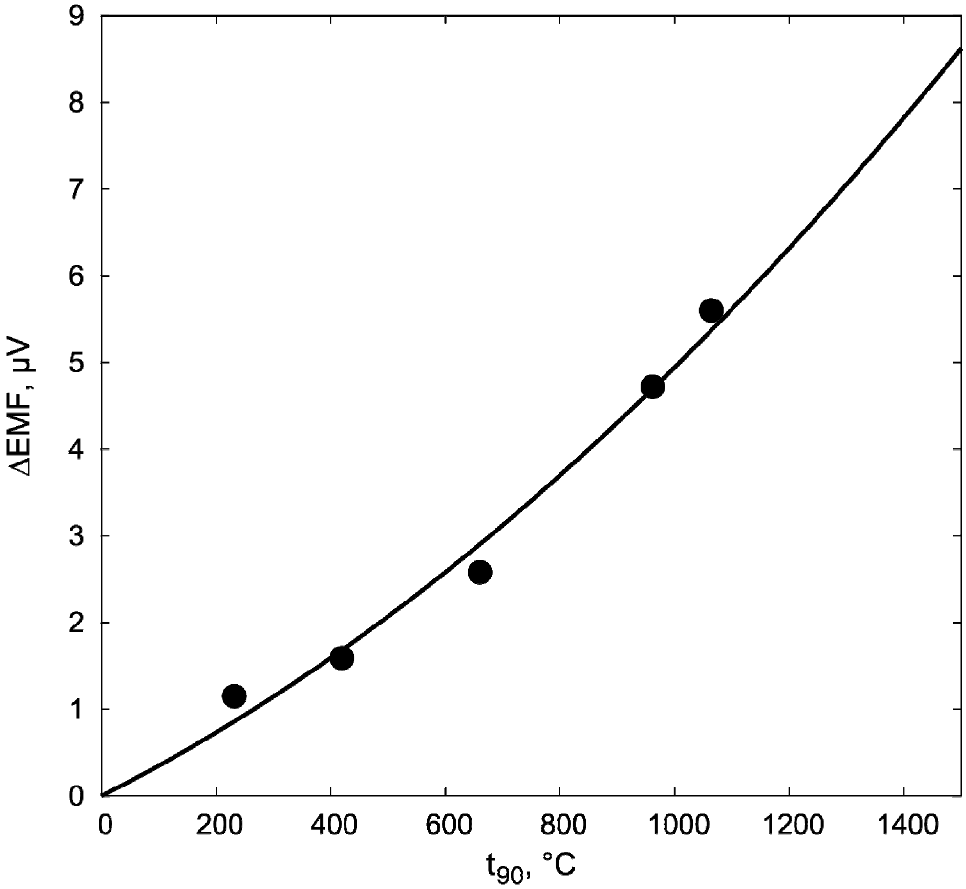
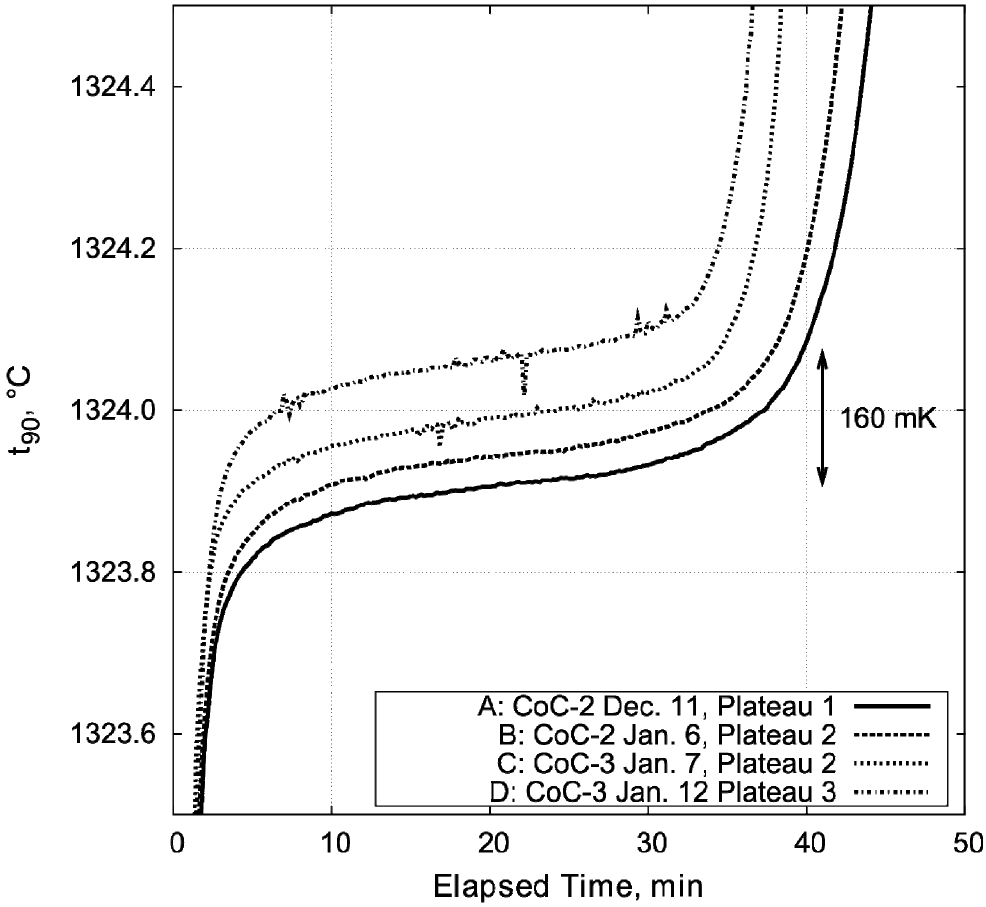
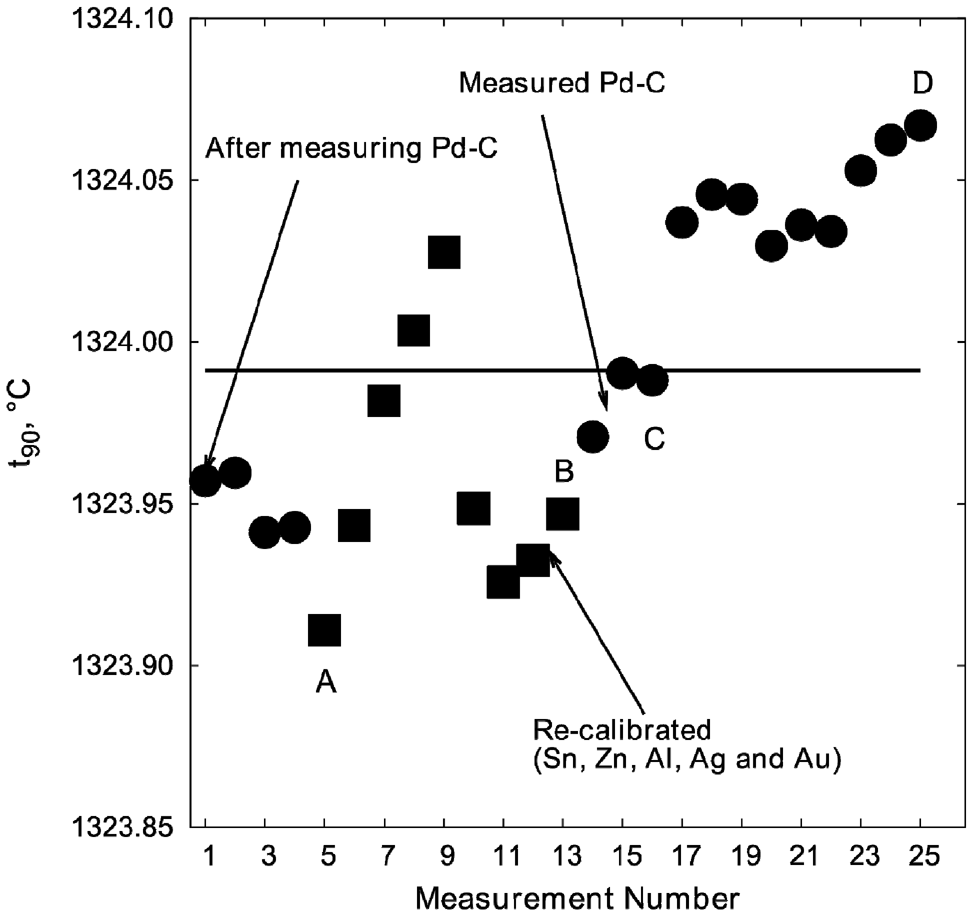


Figure 4:



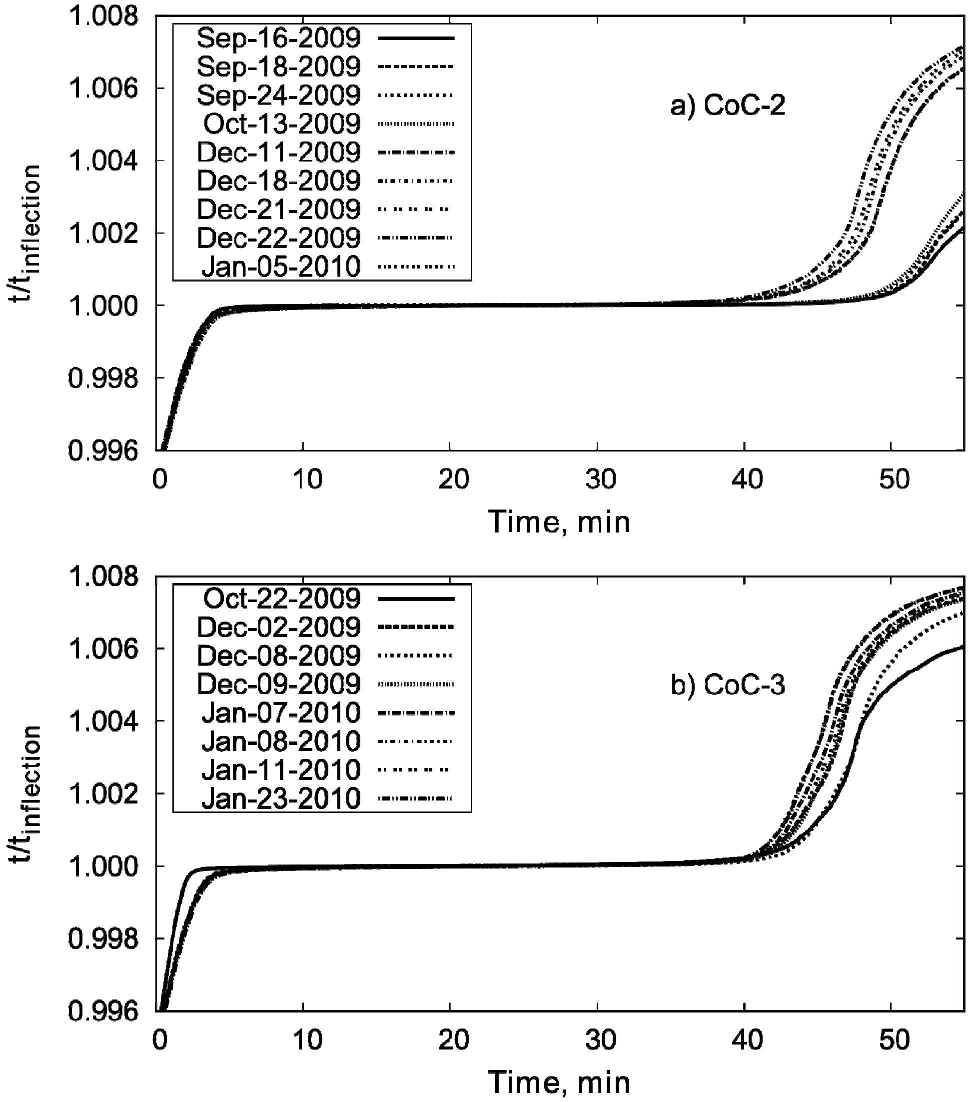
1324.4
1324.2
1324.0
1323.8
1323.6
t_{90}, °C
160 mK
A: CoC-2 Dec. 11, Plateau 1
B: CoC-2 Jan. 6, Plateau 2
C: CoC-3 Jan. 7, Plateau 2
D: CoC-3 Jan. 12 Plateau 3
0
10
20
30
40
50
Elapsed Time, min

Figure 5:



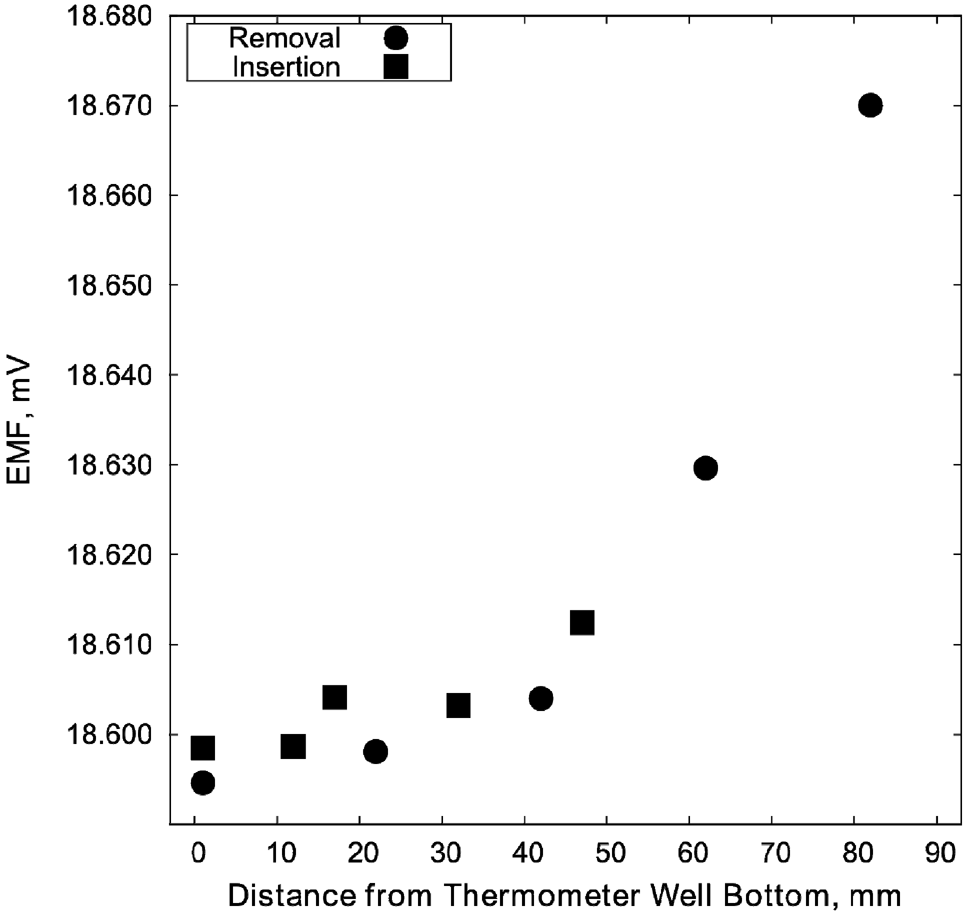
1324.10
1324.05
1324.00
1323.95
1323.90
1323.85
t_{90}, °C
Measured Pd-C
D
After measuring Pd-C
C
B
A
Re-calibrated
(Sn, Zn, Al, Ag and Au)
1 3 5 7 9 11 13 15 17 19 21 23 25
Measurement Number

Figure 6:



1.008
1.006
1.004
1.002
1.000
0.998
0.996
t/t_inflection
Sep-16-2009
Sep-18-2009
Sep-24-2009
Oct-13-2009
Dec-11-2009
Dec-18-2009
Dec-21-2009
Dec-22-2009
Jan-05-2010
a) CoC-2
0
10
20
30
40
50
Time, min
1.008
1.006
1.004
1.002
1.000
0.998
0.996
t/t_inflection
Oct-22-2009
Dec-02-2009
Dec-08-2009
Dec-09-2009
Jan-07-2010
Jan-08-2010
Jan-11-2010
Jan-23-2010
b) CoC-3
0
10
20
30
40
50
Time, min

Figure 7:


Removal
Insertion
18.680
18.670
18.660
18.650
18.640
18.630
18.620
18.610
18.600
EMF, mV
0
10
20
30
40
50
60
70
80
90
Distance from Thermometer Well Bottom, mm