

MEANS FOR MEASURING THE THERMAL QUANTITIES

LONG-TERM STABILITY OF Co-C AND Pd-C EUTECTIC FIXED POINTS FOR THERMOCOUPLES CALIBRATION

*Yasser A. Abdelaziz, Ph.D., Prof., e-mail: yasserabdefatah@yahoo.com;
F. M. Megahed, Ph.D., Prof.; M. M. Abdel-Aal, Ph.D.
National Institute for Standards, Egypt*

Abstract. Eutectic fixed points are close to becoming a reference for high temperatures calibration, especially as the new International Temperature Scale (ITS) approach to issue after the re-definition of the Kelvin unit.

In this work, the long-term stability of Co-C and Pd-C eutectic fixed points were investigated using NIS-Egypt facilities. The eutectic points were measured using Pt/Pd thermocouple. The total exposure to the Co-C and Pd-C melting temperature was about 200 h for the fixed-point cell and 150 h for the Pt/Pd thermocouple. The EMFs of the thermocouple at the melting point was observed to drift by about 0.25 °C.

Realization uncertainties were estimated to be ~ 0.446 °C for Co-C and ~0.742 for Pd-C ($k = 2$). Results show that Co-C and Pd-C eutectic cells can exhibit long-term stability.

Key words: Eutectic Fixed Points, Stability, Thermocouples, Uncertainty.

1. Introduction

For contact thermometry, Metal-carbon (M-C) eutectic fixed points represent an important development in the uncertainty of thermocouple calibration at high temperatures.

A lot of research has been carried out to verify the possibility of using eutectic points as new fixed points, some of those studies evaluated their long-term stability [1, 2 & 3]. It is important to study all other known eutectic points for longer periods, to choose the most suitable in the future as a fixed point.

Noble metal thermocouples can be used to measure temperatures up to 1600 °C without serious difficulties.

2. The Aim of the Research

In the present work, we use reference noble metal thermocouple Pt/Pd to investigate the long-term stability of the eutectic points of Co-C and Pd-C.

3. Measurement set-up

3.1. Eutectic Fixed Points

The Co-C and Pd-C cells were supplied and calibrated by NPL-UK, see cells information in Table 1. The cell design is illustrated in Fig. 1 [4]. Crucibles were made from pure graphite and they should be properly purified again after manufacturing by heating in an inert atmosphere or preferably vacuum before filling. Each cell is filled with a mixture of powder of high-purity metal and high-purity carbon. Assembled crucibles were mounted in a graphite equalizing block, in a three-zone furnace.

Table 1

Fixed points data

Parameter	Co-C	Pd-C
Supplier	NPL	NPL
Metal Purity	99.995	99.995
Graphite powder purity	99.9999	99.9999

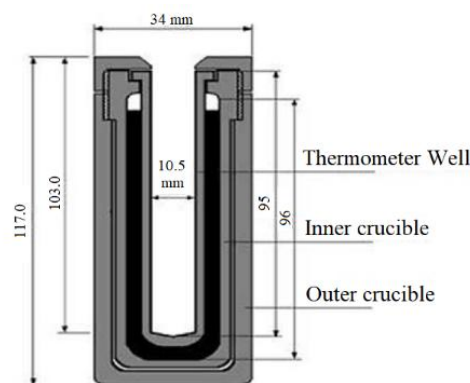


Figure 1. Design of the eutectic fixed-point cell.

3.2 Eutectic Point Furnace

A high-temperature three-zone furnace (Elite TMV16/75/610) was used in this work. Each heater of the furnace has a controller used to set the required temperature by adjusting the desired set-point and the ramp rate. The furnace is warmed to about 1316 °C for Co-C cell or 1484 °C for Pd-C cell. The approximate temperature is monitored using the furnace center zone indicator.

In this work, the temperature profile (evaluation of furnace axial homogeneity or thermal gradient) was

checked each 2 cm after furnace stabilizing over-night or until the test probe reaches stability of $< 0.1^\circ\text{C}$ for greater than 15 minutes. The profile of the eutectic point furnace was carried out at 1270°C according to the manufacturer (NPL-UK) recommendations. The furnace profile shows stability $\pm 0.39^\circ\text{C}$ at 1270°C for 10 cm immersion (eutectic furnaces are usually used with small cells). So, the above-mentioned temperature regions are convenient to locate the fixed-point cells in these regions (low gradient and uniform regions) within the furnaces.

3.3. Pt/Pd Thermocouples

Pt/Pd thermocouple was prepared and assembled at NIS-Egypt according to the international standards and recommendations [5], using 0.5 mm diameter wires with 200 cm length. All wires were supplied by Johnson Matthey as high reference-grade, (with the purity of 99.999% for platinum wire and 99.997% purity palladium wire).

The thermocouple reference junction was maintained at 0°C in a Dewar flask filled with a mixture of distilled water and crushed ice (ice bath). The reference junction was inserted for 20 cm in the ice bath using a closed-end glass tube.

3.4 Nano Voltmeter

The digital Nanovoltmeter Keithly voltmeter type-182) used in this work has internal resistance higher than $10^9 \Omega$ was used to measure emf, its resolution corresponds to temperature resolution of $1 \text{ m}^\circ\text{C}$ and 48 nV accuracy.

4. Measurement Results and Discussion

4.1. Measuring of Eutectic Fixed Points in Different Time Stages

Each Co-C and Pd-C cells were exposed for about 200 h and over 40 melting/freezing cycles in 2014, 2016, and 2018. Final tests were performed in June 2019.

The measuring of eutectic points up to 1500°C is carried out by inserting the thermocouple into a substantial ingot of Co-C and Pd-C.

The eutectic fixed point was inserted in a graphite shield (without touching the sides shield) in the most uniform region of a three-zone furnace. The cell assembly is mounted in a re-crystallized alumina tube, this assembly is completely sealed to permit a flowing argon gas atmosphere under controlled pressure. The emf output of the thermocouples used in these measurements is recorded at least every 10 seconds using a logging program.

4.2. Observed plateaus

The shapes of observed melting and freezing plateaus can use to estimate the long-term stability of the cells. Five sets of melt/freeze were realized and recorded for each cell over about 6 years. All melting plateaus are compared and plotted as shown in Fig. 2-3. There is a slight change in plateau duration and plateau shape, some of these changes may be related to the drift of the Pt/Pd thermocouple. Whereas, many previous studies have shown regression of Pt/Pd thermocouple when studying its long-term stability. As F. Edler and et al tested the thermoelectric stability of the Pt/Pd thermocouples exposed to temperatures up to about 1350°C for 250 hours, they found the Pt/Pd thermocouples stability is about $100 \text{ m}^\circ\text{C}$, measured at the freezing point of silver [6].

For, Co-C, the scatter of the melting temperature is within $\pm 4 \mu\text{V}$ ($\pm 170.5 \text{ m}^\circ\text{C}$). For Pd-C, the scatter of the melting temperature is within $\pm 2 \mu\text{V}$ ($\pm 79.1 \text{ m}^\circ\text{C}$), using calibrated Pt/Pd thermocouple, with no visible trend, which reflects the good stability for both cells and Pt/Pd thermocouple. The melting plateaus durations are about 150 sec. for Co-C and 90 sec. for Pd-C eutectic cell.

Table 2 and Fig. 4 shown an observed unexpected decrease in thermoelectric emf resulting from Co-C cell in Aug. 2015, this is mainly due to the drift of Pt/Pd thermocouple, this can be explained also from and Fig. 4, Pd-C cell, where the measurement carried out in same test days with same thermocouple, very similar change trend is observed. Here, each plot represents a plateau.

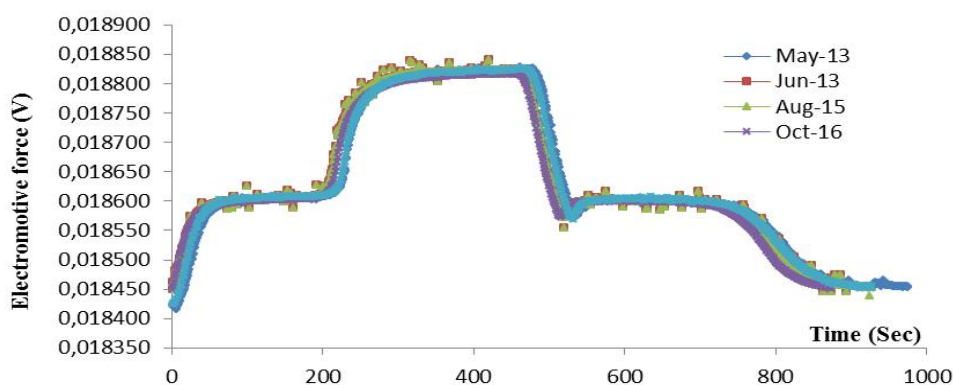


Figure 2. Melting and freezing curve of in Co-C eutectic fixed point, measured by Pt/Pd thermocouple

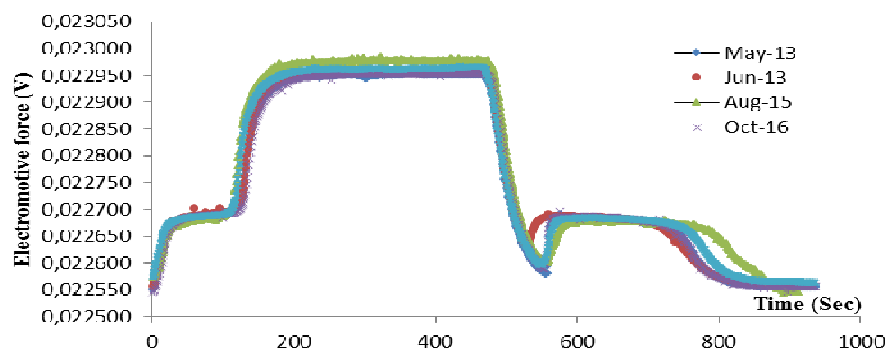


Figure 3. Melting and freezing curve of in Pd-C eutectic fixed point, measured by Pt/Pd thermocouple

Table 2

Stability results of Co-C and Pd-C eutectic fixed

Date	Co-C	Pd-C
	μV	μV
May 2013	18603.54	22688.03
June 2013	18606.00	22688.79
Aug. 2015	18604.00	22687.30
Oct. 2016	18605.32	22689.74
June 2019	18607.00	22688.37

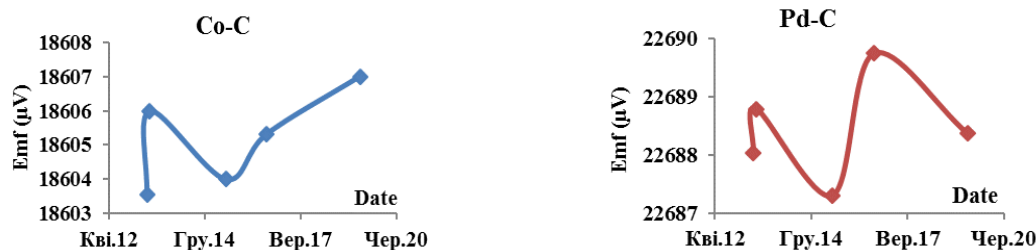


Fig. 4. Melting temperature Co-C and Pd-C cells during the test

Table 3

Pt/Pd thermocouple repeatability in Cu freezing point.

Measurement run at Cu freezing point 1084.62 °C,					$\frac{dE}{dt}$ $\mu\text{V}/^\circ\text{C}$	Repeatability	
1 st	2 nd	3 rd	4 th	5 th		μV	$^\circ\text{C}$
13276.0	13275.4	13275.2	13275.8	13275.6	20.9	0.32	0.02

4.3. Repeatability of the thermocouple at Cu freezing point

Pt/Pd thermocouples are subject to drift with use, especially at high temperatures. Where, platinum is sensitive to the presence of impurities, with which it can combine to form a eutectic alloy. High-purity protecting tubes during routine use are essential to help prevent this [7]. So, it was necessary to confirm the repeatability of Pt/Pd thermocouple using one of the ITS-90 fixed points, as a standard used for evaluating eutectic cell stability.

Table 3 shows the Pt/Pd thermocouple repeatability in emf values in the Cu freezing point. The overall repeatability is $\pm 0.32 \mu\text{V}$ ($\pm 20 \text{ m}^\circ\text{C}$).

4.4 Thermoelectric Homogeneity

The uncertainty arising from the thermoelectric inhomogeneity has a relatively large contribution to the thermocouple uncertainty at fixed points, and it is important to characterize this contribution as accurately as possible [7], the insertion/withdrawal technique was carried out at the Ag freezing point as described by McLaren and et. al. [8].

In this technique, the thermocouple was inserted slowly into the cell after initiating the freeze and its measuring junction was positioned 2 cm below the surface of the metal. The thermocouple was held at this location for 15 min and then its emf was measured. The

immersion of the thermocouple was then increased by 2 cm and after 5 min its emf was again measured.

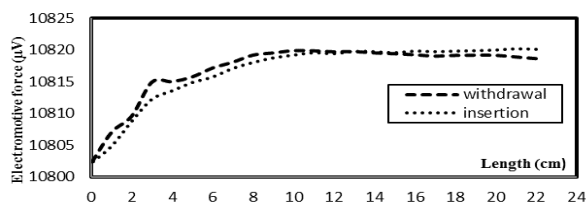


Figure 5. Thermoelectric homogeneity test of Pt/Pd thermocouple

This procedure was repeated until the thermocouple was fully immersed in the freezing point cell. After it was held at full immersion for about 15 min, its emf was measured. It was then withdrawn from the cell at the rate of 2 cm per min and its emf was measured while its measuring junction was held at each of the immersion locations used during insertion. The obtained results are presented in Figure 5.

The profile indicates inhomogeneity equivalent in temperature to ~ 41.7 m°C. This may be due to the reason that the stress-relieving coil has the measurable effect that decreased with the fixed-point temperature increase [7]. These results demonstrate that about 11 cm of immersion is required in the fixed-point cell to overcome thermal conduction effects.

4.5. Uncertainty of measurements

Uncertainties of measurement calculated following EA guide ‘Expression of the Uncertainty of Measurement in Calibration EA-4/02’ [8]. The uncertainty budget of the thermocouple at eutectic fixed points incorporating the various contributory factors is shown in Table 4.

Uncertainties for the items labeled repeatability are typically evaluated as Type A uncertainties, using statistical methods. The other items are primarily evaluated using Type B methods. The combined uncertainty U_C is expressed in the form of a 95% confidence level ($k=2$). All uncertainty sources are described in the previous sections.

Table 4

Uncertainty budget of thermocouple type Pt/Pd in eutectic fixed points

Expected components of uncertainty	Fixed point ingots, μV	
	Co C	Pd C
Statistical standard uncertainty	0.64	0.41
Determination of the fixed-point temperature	5.192	9.361
Voltmeter calibration	0.38	0.38
Voltmeter resolution	5.77 E-06	5.77 E-06
Voltmeter drift	0.0577	0.0577
Thermocouple homogeneity @ Ag freezing point, see section 3.4	0.4619	0.4619
Reference junction	0.1529	0.1529
Combined standard uncertainty U_C , μV	5.268	9.390
Corresponding Combined uncertainty U_C, °C	0.223	0.371
Expanded uncertainty U @ ($k=2$), °C	0.446	0.742

5. Conclusion

There are not many publications on the long-term stability of Eutectic fixed points, especially studies over several working years. This is due to the difficulties of measurement at the high temperatures involved. In this work the Co-C and Pd-C cells have been investigated for long-term stability (along 6 years), a slight increase appeared in melting values after about 200 h and over 40 melting/freezing cycles.

The temperature drifts observed for the Co-C cell is within ± 4 μV (± 170.5 m°C), but for Pd-C, is within ± 2 μV (± 79.1 m°C), using calibrated Pt/Pd thermocouple.

The uncertainty of the realization of Co-C and Pd-C eutectic fixed points was estimated to be approximately 0.446 °C for Co-C and 0.742 for Pd-C (@ $k = 2$).

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