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An Investigation of the Thermoelectric Properties of Type S, Type R and Pt/Pd Thermocouples in Eutectic Fixed Points

[1] Yasser A. Abdelaziz, [1] F. M. Megahed, [2] H. M. Hashem, [1] M. M.Abdel-Aal and [2] M. Hammam

[1] National Institute for Standards, Giza, Egypt
[2] Department of physics, faculty of science, Helwan University, Egypt
[1] Tel.: +201005790620, fax: +202 33867451
E-mail: yasserabdelfatah@yahoo.com

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Abstract: This work presents an investigation of the thermoelectric properties of the Type S, Type R and Pt/Pd thermocouples up to high temperature using eutectic fixed points, including evaluation of the fixed-points EMF, thermoelectric inhomogeneity and repeatability of these thermocouples. All used thermocouples were assembled and prepared using NIS-Egypt capabilities according to the international recommendation. This work can provide information either on the behavior of the mentioned thermocouples at high temperature eutectic fixed points using and its proper usage for the precise measurement of temperature in this temperature range.

Keywords: Thermocouples, Eutectic fixed points, Thermoelectric properties.

1. Introduction

Thermocouples are the most commonly used thermometers at high temperature in research and industrial application because of their ability to carry out an accurate temperature measurement. The present international scale ITS-90 [1] replaced it to high temperature platinum resistance thermometers HTSPRTs.

But HTSPRTs are not only fragile and expensive, they also need high-resolution readout instruments to make high precise temperature measurements and should not be used in a metal block at high temperatures due to likely contamination of the sensor. Noble metal thermocouples can be used to measure temperatures up to 1600 °C without serious difficulties, taking into consideration that their efficient use requires more studies of their thermoelectric properties to determine the most appropriate in this range of temperatures.

For contact thermometry, Metal-carbon (M-C) eutectic fixed points are offering a step change improvement in calibration uncertainty, as well as opening up the possibility of calibrating high temperature thermocouples.

In the present work we use the eutectic points of Co-C and Pd-C to study the thermoelectric properties of some noble metal thermocouples Types S, R and Pt/Pd as thermoelectric inhomogeneity, stability and repeatability.

2. Experimental Details

2.1. Eutectic Fixed Points

The basic design of metal-carbon eutectic cells illustrated in the Fig. 1 [2]. Crucibles are made from pure graphite (0.999 995 or better) and they should be properly purified again after manufacturing. The inner diameter of the crucible was 25 mm and the thickness of the wall was 8 mm. The inner diameter of the thermocouple well was 10.5 mm. Thermal modeling suggests that this extra thickness of graphite will result in some rounding of the measured melting curve, because the thermocouple will take longer to reach thermal equilibrium with the liquid-solid interface. In addition it may be advisable to further purify by heating in an inert atmosphere or preferably vacuum prior to filling.

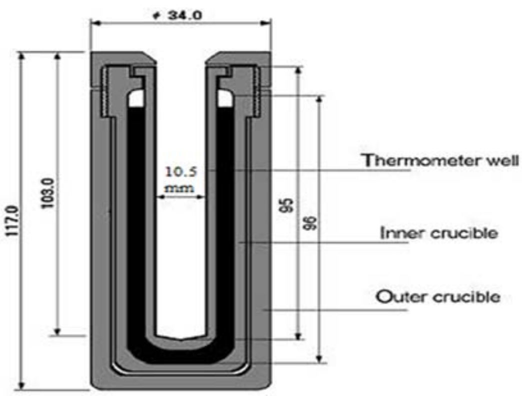

Fig. 1. Design of eutectic fixed-point cell.

Crucible purification is even more important with eutectic fixed-points than with the standard pure metal fixed-points. This is because the crucible wall partially dissolves in the ingot and any impurities in the graphite will contaminate the fixed point. The cell is filled with a mix of high-purity metal and high-purity carbon powders. Care is taken to maintain the purity of the metal and graphite powders by filling the cell in an argon atmosphere and by careful preparation and handling. The cell is then heated to just above the melting temperature of the eutectic, then cooled, refilled with additional powder and reheated. The crucible was mounted in a graphite equalizing block, in a three-zone furnace.

2.2. Eutectic Point Furnaces

A suitable furnace (Elite TMV16/75/610) should be used. For realization of the eutectic fixed points a three heater zones furnace is used. Each heater has a controller used to set to the required temperature by adjusting the desired set-point and the ramp rate. Note that a ramp rate of 5 °C/min must never be exceeded [3]. On the morning of the day of use the argon gas pressure in the worktube is set to a minimum of 1.02 atm. The furnace is warmed to about 1316 °C (Co-C) or 1484 °C (Pd-C) (actual temperatures, not set-point temperatures), using a ramp rate of 5 °C/min up to the set-point. This procedure takes approximately 4 h. The approximate temperature is monitored using the furnace center zone indicator.

2.3. Thermocouples Preparation

Thermocouples type Pt-10 % Rh/Pt (Type S), Pt-13 % Rh/Pt (Type R) and Pt/Pd were prepared using NIS-Egypt capabilities from Pt, Pt-10 % Rh, 13 % Rh/Pt and Pd wires, with 0.5 mm in diameter and 200 cm length. All wires were purchased from Johnson Matthey as reference grade, where the platinum wire of 99.999 % purity and palladium wire of 99.997 % purity. The Pt, Pt-10 % Rh, 13 % Rh/Pt and Pd wires were first annealed electrically at 1300 ºC for approximately 10 hours, cooled rapidly to room temperature and then annealed for one hour at about 450 ºC to reduce the lattice vacancies that may be quenched into the wires during cooling from the high temperature anneal [3]. The annealed wires were assembled by threading the thermoelements into the bores of a twin bore high purity alumina tube with overall diameter 4.5 mm and length 70 cm. Before use all alumina tubes were baked at 1200 ºC.

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

2.4. Nano Voltmeter

Digital Nanovoltmeter (Keithly voltmeter type-182) with internal resistance higher than 109 Ω was used to measure EMF, its resolution corresponds to temperature resolution of 1 mK and 48 nV accuracy.

3. Results and Discussion

3.1. Eutectic Fixed Points Calibration

The calibration of noble metal thermocouples up to 1500 ºC is carried out by inserting the thermocouple into a substantial ingot of Co-C and Pd-C. This is encased in a very pure graphite crucible. Prior to use the ingot assembly is placed in a hollow graphite shield (mounted on a disk of graphite felt and not touching the shield at the sides) in the most uniform region of a three zone furnace. This arrangement is mounted on an alumina brick in a re-crystallized alumina tube, which is sealed to permit a continuously flowing argon gas atmosphere with a controlled pressure [4].

The EMF output of this thermocouple is recorded at least every 10 seconds by a computer logging program as shown in Figs. 2, 3, 4, 5, 6 and 7. To start the melt, the furnace is warmed to 1332 °C for (Co-C) cell or 1500 °C for (Pd-C) cell, with a ramp rate of 5 °C/min. The melting takes place at approximately 1324.29 °C (Co-C), or 1491.5 °C (Pd-C), with a melting range of around 0.2 °C. On completion of melting, the temperature will rise to a plateau corresponding to the furnace set-point. The melting occurs over a range of approximately 0.2 °C. The convention is that the fixed point EMF is given by the point of inflection of the melting curve. It is therefore necessary to fit a 3rd order polynomial to the melting curve, and evaluate the EMF where the second derivative of the polynomial is equal to zero.

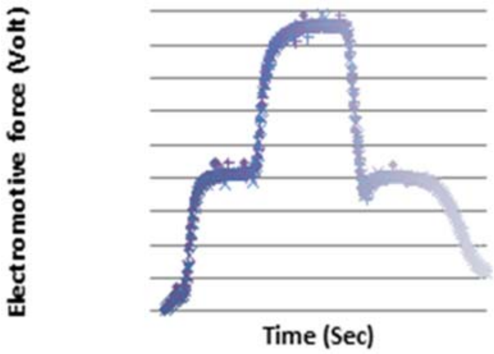

Fig. 2. Melting and freezing plateaus of Co-C eutectic fixed point using Type S thermocouple.

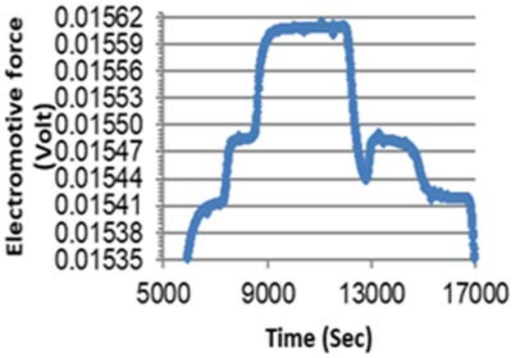

Fig. 3. Melting and freezing plateaus of Pd-C eutectic fixed point using Type S thermocouple.

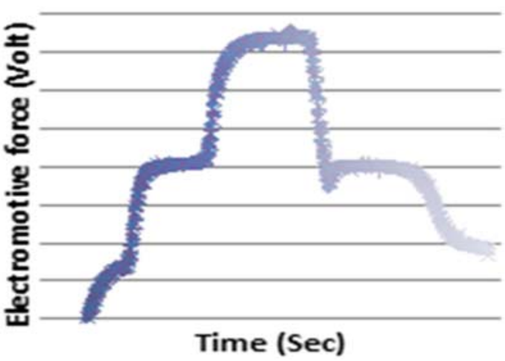

Fig. 4. Melting and freezing plateaus Co-C eutectic fixed point using Type R thermocouple.

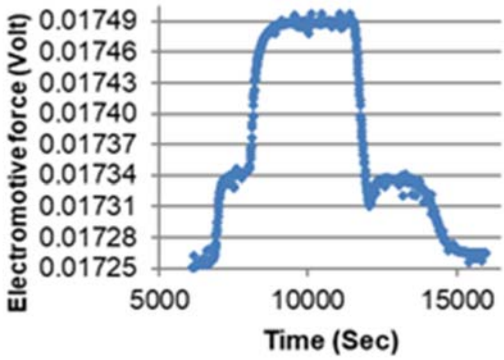

Fig. 5. Melting and freezing plateaus of Pd-C eutectic fixed-point Type R thermocouple.

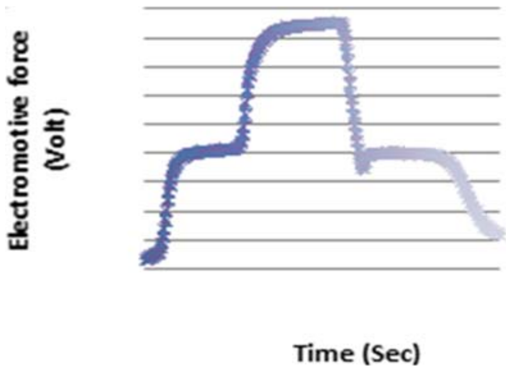

Fig. 6. Melting and freezing plateaus of Co-C eutectic fixed point using Pt/Pd thermocouple.

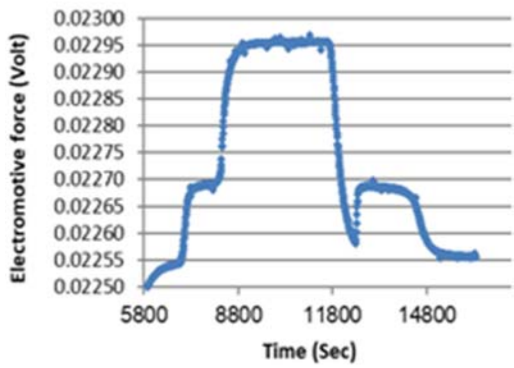

Fig. 7. Melting and freezing plateaus of Pd-C eutectic fixed point using Pt/Pd thermocouple.

The following Tables 1, 2 and 3 shows the melting point values of Co-C and Pd-C eutectic points, (E) measured EMF, sensitivity coefficient, (E_{ref}) the corresponding reference value of fixed point, ΔE (difference between reference value and measured value ($\Delta E = E_{ref} - E$), (ΔT) difference in °C.

3.2. Thermoelectric Homogeneity

To test the thermoelectric homogeneity of the thermocouple wires used in the present work (4).

Table 1. Thermo EMF of Type S thermocouple in the melting points of Co-C &Pd-C eutectic cells.

Fixed point ingot	M.P. Value °C	Measured EMF E µV	dE/dt µV/°C	Refer. Values E_{ref} µV	ΔE= E_{ref}- E µV	Cores. Temp. Δ T °C
CoC	1324.29	13453.4	12.135	13453.74	0.34	0.028
PdC	1491.50	15486.0	12.049	15479.30	-6.7	-0.556

Table 2. Thermo EMF of Type R thermocouple in the melting points of Co-C & Pd-C eutectic cells.

Fixed point ingot	M.P. Value °C	Measured EMF E µV	dE/dt µV/°C	Refer. Values E_{ref} µV	ΔE= E_{ref}- E µV	Cores. Temp. Δ T °C
CoC	1324.29	14963.9	14.102	14971.00	7.10	0.504
PdC	1491.50	17341.6	14.074	17331.07	-10.53	-0.748

Table 3. Thermo EMF of Pt/Pd thermocouple in the melting points of Co-C & Pd-C eutectic cells.

Fixed point ingot	M.P. Value °C	Measured EMF E µV	dE/dt µV/°C	Refer. Values E_{ref} µV	ΔE= E_{ref}- E µV	Cores. Temp. Δ T °C
CoC	1324.29	18604.9	23.6	18628.44	23.54	0.998
PdC	1491.50	22689.7	25.3	22716.95	27.25	1.077

The insertion/withdrawal technique was carried out for Pt-10 % Rh/Pt (Type S), Pt-13 % Rh/Pt (Type R) and Pt/Pd thermocouples at the freezing point of Ag using the sealed cells supplied by NPL-England. This method was described in detail by McLaren and Murdock and by Burns, *et al.* [5, 6 and 7]. In this technique after initiating the freeze in the freezing point cells, the thermocouple was inserted slowly into the cell 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. This procedure was repeated until the thermocouple was fully immersed in 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 the Figs.8, 9 and 10.

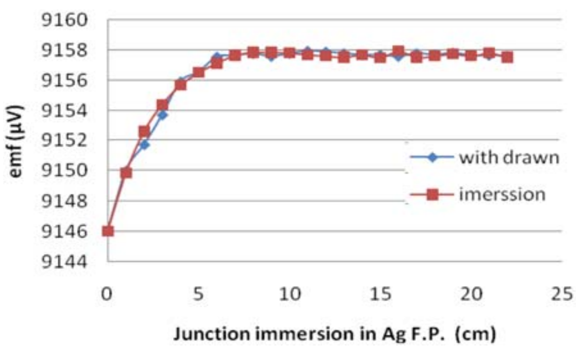

Fig. 8. Thermoelectric homogeneity test of Type S thermocouple.

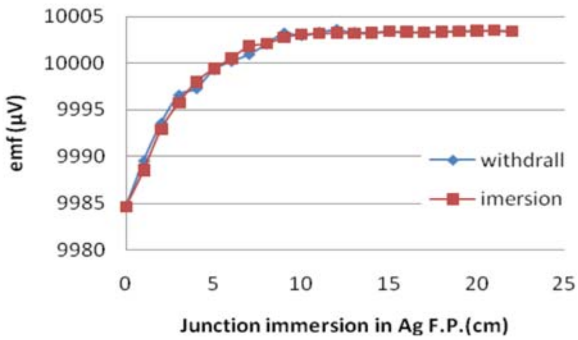

Fig. 9. Thermoelectric homogeneity test of Type R thermocouple.

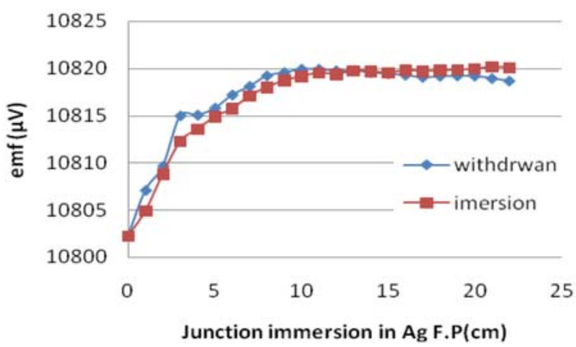

Fig. 10. Thermoelectric homogeneity test of Pt/Pd thermocouple.

The immersion/withdrawal profiles for Type S, Type R and Pt/Pd thermocouples at freezing point of Ag nearly coincide and from thermal conduction threshold to maximum immersion indicate thermoelectric inhomogeneity along the elements equivalent in temperature to ≤ 50 mK in Ag point.

3.3. Repeatability of Thermocouples at Eutectic Points

The thermocouples were place in eutectic fixed points (Co-C and Pd-C). Tables 4 and 5 shows the repeatability in EMF values with time in the fixed points [8]. The fixed-point EMF of all the thermocouples decreased with time, as one normally expects. After 5th run in fixed points, most thermocouples showed a Variable change in EMF by about from 1 to 5 µV, but the Pt/Pd thermocouple shown a better repeatability.

Table 4. Repeatability of thermocouples at Co-C eutectic cells.

T/C (Co-C)	1st	2nd	3rd	4th	5th	Avr.	µV/°C	Repeatability	
1324.29 °C	µV							µV	°C
S	13453.9	13453.5	13453	13453.4	13453.2	13453.4	12.135	**0.34**	**0.03**
R	14964	14963.6	14963.8	14964.1	14964.1	14963.9	14.102	**0.22**	**0.02**
PT/Pd	18603	18605.3	18605.1	18605	18606	18604.9	23.6	**1.12**	**0.05**

Table 5. Repeatability of thermocouples at Pd-C eutectic cells.

T/C (Pd-C)	1st	2nd	3rd	4th	5th	Avr.	µV/°C	Repeatability	
1491.5 °C	µV							µV	°C
S	15488.4	15488.5	15483.1	15484.7	15485.1	15486.0	12.049	**2.39**	**0.20**
R	17345.1	17341.1	17340.9	17340.8	17340.2	17341.6	14.074	**1.97**	**0.14**
PT/Pd	22688.9	22689.2	22690.2	22690.1	22690.3	22689.7	25.3	**0.64**	**0.03**

3.4. EMF - Temperature Relation of Type S and R Thermocouples up to 1500 °C

In the temperature range up to 1500 °C, we used the standard reference function suggested by Burns, *et al.* [7] for calibration and interpolation calculations between measured data

$$E_{ref} = b_0 + \sum_{i=1}^{N} b_i t_{90}^i \quad (1)$$

These calculations were carried out as follow:

1) The EMF deviations (Δ EMF) resulting from the subtracting of the reference function EMFs from the measured EMFs were fitted with quadratic polynomial.

2) The coefficients of the deviation function are added to those of the reference function to give the coefficients of the calibration function for the thermocouple used in this work.

3) For the derivation of the coefficients of the deviation function in the range up to 1500 °C we have used the EMFs of the Type S and Type R thermocouples at the freezing point of Ag and eutectic points of Co-C and Pd-C. The coefficients in Equation (1) for our thermocouple were calculated and are given in Table 6.

Table 6. Calculated coefficients of Type R and S thermocouple.

Calibration Point °C	Type R Thermocouple		Type S Thermocouple	
	Measured EMF µV	Reference EMF - Measured EMF (Δ EMF) µV	Measured EMF µV	Reference EMF - Measured EMF (Δ EMF) µV
Ag; 961.78 Co-C; 1324.29 Pd-C; 1491.5	10003.39 14963.91 17341.8	0.04 7.09 -9.73	10808.9 18605.11 22690.23	4.18 23.33 26.72
	Deviation Coefficients: Δ c(1) = 4.98883686 Δ c(2) = -2.03768676 E-03 Corrected Coefficients: c(0) = 2.95157925 E03 c(1) = 2.46822435 E00 c(2) = 1.39187634 E-02 c(3) = -7.6408595 E-06 c(4) = 2.05305291 E-09 c(5) = -2.9335967 E-13		Deviation Coefficients: Δ c(1) = 2.26047061 Δ c(2) = -9.26484514 E-04 Corrected Coefficients: c(0) = 1.32900444 E03 c(1) = 5.60556373 E00 c(2) = 5.62156741 E-03 c(3) = -1.6485626 E-06 c(4) = 1.29989605 E-11	

4. Uncertainty Evaluation

Uncertainties of measurement shall be calculated in accordance with EA publication EA-4/02 'Expression of the Uncertainty of Measurement' in Table 8 Uncertainty budget of thermocouple Type R in eutectic fixed points calibration [9]. The uncertainty budget of all thermocouples at eutectic fixed points incorporating the various contributory factors is shown in Tables 7, 8 and 9.

Table 7. Uncertainty budget of thermocouple Type S in eutectic fixed points.

Expected components of Uncertainty	Fixed point ingots	
	Co C	**Pd C**
	µV	
Statistical standard uncertainty	0.34	2.39
Determination of the calibration fixed point temperature	2.6686	4.4585
Drifts of the means used to determine the calibration fixed point	0.1187	1.0174
Voltmeter calibration	0.38	0.38
Voltmeter resolution	5.77E-06	5.77E-06
Voltmeter drift	0.05773	0.05773
Thermocouple homogeneity	0.2483	0.2483
Reference junction	0.1443	0.1443
Combined standard uncertainty U_C (µV)	2.7352	5.1822
Corresponding Combined uncertainty U_C in °C	**0.2255**	**0.4300**
Expanded uncertainty U, k=2 (°C)	**0.4510**	**0.8601**

Table 8. Uncertainty budget of thermocouple Type R in eutectic fixed points.

Expected components of Uncertainty	Fixed point ingots	
	Co C	**Pd C**
	µV	
Statistical standard uncertainty	0.22	1.97
Determination of the calibration fixed point temperature	3.102	5.2059
Drifts of the means used to determine the calibration fixed point	0.1380	1.1880
Voltmeter calibration	0.38	0.38
Voltmeter resolution	5.77E-06	5.77E-06
Voltmeter drift	0.0577	0.0577
Thermocouple homogeneity	0.2425	0.2425
Reference junction	0.1443	0.1443
Combined standard uncertainty U_C (µV)	3.1491	5.7115
Corresponding Combined uncertainty U_C in °C	**0.2233**	**0.4059**
Expanded uncertainty U, k=2 (°C)	**0.4467**	**0.8119**

Table 9. Uncertainty budget of thermocouple Type Pt/Pd in eutectic fixed points.

Expected components of Uncertainty	Fixed point ingots	
	Co C	**Pd C**
	µV	
Statistical standard uncertainty	1.12	0.64
Determination of the calibration fixed point temperature	5.1920	9.3610
Drifts of the means used to determine the calibration fixed point	0.2309	2.1361
Voltmeter calibration	0.38	0.38
Voltmeter resolution	5.77E-06	5.77E-06
Voltmeter drift	0.0577	0.0577
Thermocouple homogeneity	0.4619	0.4619
Reference junction	0.1530	0.1530
Combined standard uncertainty U_C (µV)	5.3525	9.6429
Corresponding Combined uncertainty U_C in °C	**0.2268**	**0.3811**
Expanded uncertainty U, k=2 (°C)	**0.4536**	**0.7623**

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 major contribution to the uncertainty is attributed by inhomogeneity of thermocouple has been estimated from the immersion profile of the fixed points observed during the measurement. The uncertainty due to purity of ingots was evaluated using its certificate. The thermocouple drift was estimated from the earlier fixed point measurements. Other uncertainty sources, related electrical measuring system, are included in the total uncertainty budget as digital voltmeter and reference junction. The combined uncertainty UC expressed in the form of 95 % confidence level.

5. Conclusion

The present study on the Type S, Type R and Pt/Pd thermocouples fully justifies that all this thermocouples are nearly coincide up to high temperature using eutectic fixed points (Co-C and Pd-C). But from uncertainty and accuracy point of view Pt/Pd thermocouple appears as a good alternative for the thermocouples Type S, Type R in the temperature range up to 1500 °C.

It is demonstrated in this work that the Type S, Type R and Pt/Pd thermocouples, following suitable high temperature annealing is capable of repeatability of less than 50 mK at Co-C and Pd-C eutectic fixed points.

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