

**High temperature sensors with self-calibrating capabilities:
Abstract and Summary Report**

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abstract and summary report

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Approved on behalf of NPLML by Leon Rogers, Group Leader, Temperature &
Humidity.

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1 ABSTRACT

The design, construction and testing of self-validating thermocouples using high temperature fixed-points (HTFPs) has been successfully completed. In particular, the miniaturisation of HTFPs, to a level where *in-situ* measurements can be made, has been shown possible, while still providing suitable immersion for clear observation of the melting and freezing plateaus.

The self-validating thermocouple consists of two main parts: a W-Re thermocouple and a HTFP cell. The HTFP cell contains a eutectic alloy of a metal and carbon. Four different alloys were chosen for this study: cobalt-carbon (Co-C), platinum-carbon (Pt-C), ruthenium-carbon (Ru-C) and iridium-carbon (Ir-C).

The self-validating thermocouples were constructed with two designs – containing one ingot (the “single-cells”) and two ingots (the “multi-cells”). Each were based upon the following HTFPs (where the nominal melting temperature is given in brackets):

Single-cells: Co-C (~1324 °C), Pt-C (~1738 °C), Ru-C (~1953 °C) and Ir-C (~2289 °C)
Multi-cells: “Co-C & Pt-C”, and “Pt-C & Ru-C”

During construction, it was found that some of the cells showed hairline cracks on the outside of the graphite crucible. Construction and tests continued, and the cracks did not become significant enough to cause any operational issues. The exception was the Co-C & Pt-C multi-cell which was not robust enough to withstand the tests. This was investigated and found to be due to severe erosion of the graphite walls. Until further investigations can be made, it is recommended that the difference between the transition temperatures of the two HTFPs within a multi-cell should be kept to a minimum.

Thermal cycling of the single-cells was completed successfully and the thermocouple output at the resulting melt and freeze plateaus were calculated and plotted. The results showed that these (even after a single cycle) fall outside the temperature assignment uncertainty of the HTFP. Thermal endurance of these cells showed that the Ir-C self-validating thermocouple was severely affected, drifting by ~88 °C over 10 h exposure.

Thermal cycling and an endurance test of the multi-cell Pt-C & Ru-C were completed successfully – the reduced ingot size and the poorer immersion characteristics did not impair the observation of the melting and freezing plateaus.

Melting temperatures and uncertainties, traceable to NPL’s realisation of the International Temperature Scale of 1990 (ITS-90) have been determined for the HTFP cells alone by radiation thermometry. This was completed for all the single-cells, both before and after the thermal tests. Comparing the results before and after showed no significant change in the cell performance – and therefore all drifts observed during the thermal tests were due to the thermocouple and can be corrected for with confidence.

Traceable temperatures were also assigned by radiation thermometry to the Pt-C & Ru-C multi-cell after the thermal tests were complete. These showed an increase in the assigned melting temperature (when compared to the equivalent single cells) of ~2 °C. This suggests that in this measurement set-up, the measurement of the multi-cell melting temperatures were influenced by the furnace temperature.

The four stages of a simple user procedure for implementing thermocouple drift correction are given and two examples of different scenarios are discussed. The single-cells are suitable for monitoring and correcting the drift over a narrow temperature range, whereas the multi-cells (where the HTFP temperatures are chosen to be above and below the range of interest) are suitable for monitoring and correcting the drift over a wide temperature range.

In summary, the designs for self-validation of thermocouples developed within this project were successful. The measurements have shown that Type C (W-Re) thermocouples can drift significantly at high temperatures, even over the short time periods used here (1 h – 10 h) and that this design of a self-validating thermocouple is suitable for such *in-situ* observation. Self-validation is therefore important to improve the confidence in W-Re thermocouple measurements above 1300 °C (and also for base metal thermocouples at lower temperatures).

2 SUMMARY REPORT

This document provides a short background and introduction to the project: “High temperature sensors with self-calibrating capabilities”. A summary of the objectives, the technical method, the results and findings of the project is then given.

Please note that within this document, the pairing of the W-Re thermocouple and the high-temperature fixed-point cell will be referred to as the “self-validating” thermocouple. In the original project documentation, they are referred to as a “self-calibrating” thermocouple.

In addition to this public-access summary, NPL have also provided a public-access User Manual (NPL Report ENG 38, ISSN: 1754-2987).

2.1 BACKGROUND

High temperature contact thermometry sensors (above 1300 °C) are used by a wide spectrum of industries (e.g. ceramics, glass, carbon composites, nuclear fuel manufacture) as well as for research applications.

If one needs to measure temperatures in excess of 1600 °C, then thermocouples must be constructed of refractory materials. However, these are beset with application problems – for example chemical reactions between the materials from which the thermocouple is constructed cause rapid decalibration which is observed during use. By far the most widely available thermocouple for measurements in this temperature range is the tungsten-rhenium (W-Re) thermocouple. Noble metal alternatives are available in part of the range e.g. rhodium-iridium thermocouples, but these are, in general, too expensive for all but the most specialised applications.

The problem of decalibration, or drift, which is typically very significant for tungsten-rhenium thermocouples affects the accuracy and efficiency of temperature measurement and process control. It is therefore desirable to validate the performance of the thermocouple (re-calibrate) and if possible, undertake this validation *in-situ*. Removal of such thermocouples for recalibration is impractical for example, due to embrittlement or use in hostile environments. Driftless sensors, drift mitigation, or *in-situ* validation methods would bring about a step change improvement to temperature measurement with refractory thermocouples [1]. Such capability would allow users to run processes with greater energy efficiency, reduce waste, and operate with tighter tolerances. They will also allow for more reliable temperature measurement where removal and replacement of sensors is impractical.

The requirements for improved high temperature contact thermometry were identified from a variety of sources, by direct questioning of calibration laboratories, sensor manufacturers and possible high temperature measurement users in industry. Documentary sources were also examined, in particular the IEC standard for W-Re thermocouples currently in development and the European Virtual Institute for Gas Turbine Sensors. In addition an industrially focussed workshop was held on 9th March 2011 at ESTEC, Noordwijk. The following sectors were represented at that workshop: aerospace, space, metal production, sensor manufacturers, and nuclear power.

2.1.1 Concept of self-validation

The conventional calibration of thermocouples uses known temperature references. For the highest performance these are generally large ingots of a defining ITS-90 fixed-point (e.g. freezing temperature of Zn, Ag or Cu). The size of the fixed-point cell is usually considerable: >10 cm in length and containing about 1 kg of high purity metal. They require tightly controlled thermal environmental conditions and are only suitable for use in a laboratory environment.

However, the concept of using fixed-points can be adapted for validating the performance of a thermocouple *in-situ*. This can be done through miniaturising the fixed-point, and incorporating it as part of the measurement junction of the thermocouple. In so doing the performance of the thermocouple can be evaluated without need for removal of the sensor for recalibration. Miniature fixed-points for thermocouple *in-situ* validation have been studied in the past, but at lower temperatures than those envisaged here.

The limiting factor of prior approaches to fixed-point crucibles for self-validation was that alumina crucibles were used; these are brittle and difficult to machine, and are limited by the melting temperature of the ceramic. These limitations can be overcome by employing metal-carbon eutectic binary alloys in graphite crucibles – which are generally known as high-temperature fixed points (HTFPs).

For the purposes of this document we define a HTFP as a fixed-point operating above the Cu fixed-point (1084 °C) and based on binary alloys of metal and carbon. Research into HTFPs for calibration of both non-contact and contact thermometers has advanced rapidly since the realisation that the suppression of the melting temperature by contamination with graphite could be used to create a new generation of fixed points based on metal-carbon eutectic alloys and variants [2, 3]. Table 1 lists the reported metal-carbon eutectic fixed-points investigated to date, with their nominal transition temperatures. The performance of these HTFPs alone has been very well characterised by radiation thermometry. The temperature repeatability, i.e. the measured temperature of repeated melts, for all the HTFPs is excellent, better than 0.05 °C from melt to melt [3]. The reproducibility (agreement between cells from different suppliers) is somewhat worse but huge improvements have been made recently so that reproducibility for the best cells, those made of Co-C, Pt-C and Re-C are repeatable to ~0.01 °C, which is at the limit of current measurement capability [4-6].

Eutectic	Approximate temperature / °C
Fe-C	1153
Co-C	1324
Ni-C	1329
Pd-C	1492
Rh-C	1657
Pt-C	1738
Ru-C	1953
Ir-C	2289
Re-C	2474

Table 1: Metal-carbon eutectics with approximate melting temperatures [3, 4, 7].

2.1.2 HTFPs for thermocouple calibration

Although initially developed for radiation thermometry applications, HTFPs are also having a significant impact on high temperature thermocouple thermometry. There is already a strong body of research underway around the world that is establishing Co-C and Pd-C as fixed-points for noble metal thermocouple calibration at high temperatures [8-11].

In the next few years, when temperatures are assigned to the HTFPs, these two HTFPs will supplant the currently established Pd wire-bridge method of calibration. The reasons for this are threefold: a) the Co-C point is mid-way between the Cu point and the Pd wire bridge point and so is ideally located to identify any interpolation problems with thermocouples, b) the wire bridge method involves destruction of the measuring junction of the thermocouple, not necessary for an ingot based technique, and c) the uncertainty around the highest temperature will be routinely around 2 and 3 times lower than is possible with the wire bridge method [8,11,12]. A final advantage is that use of the Pd-C point (1492 °C) will give access to the superior performance of the pure element Pt/Pd thermocouple at the upper end of its

operating range. Until now this has not been possible because the Pd wire-point was the only means of calibrating such thermocouples.

The initial technical challenges associated with the Pd-C fixed-point have now been overcome [13]. Within the UK, the National Physical Laboratory (NPL) already has ISO 17025 (UKAS) accredited calibration capability at the Co-C and Pd-C points and is supplying noble metal thermocouples calibrated with an uncertainty of $\sim 0.5\text{ }^{\circ}\text{C}$ (coverage factor $k = 2$) at those temperatures. A temperature is assigned to both HTFPs by radiation thermometry [14]. The Co-C HTFP has already been installed in an industrial setting [12] and has been operating continuously and reliably for over 2 years. Regular monitoring indicates the absence of drift of this HTFP.

HTFPs are available above the temperature range of Type R, S, and B noble metal thermocouples. These HTFPs can be used for the calibration of refractory metal thermocouples such as the W-Re Types C and D, and trials have already been performed in this area with large HTFP ingots [15-17].

2.1.3 Use of HTFPs for thermocouple self-validation

Recently there has been a strong resurgence of interest in self-validating sensors for hostile industrial and space-based applications [16, 18]. Generally these are being developed to overcome the drift of sensors at very high temperatures (above $1100\text{ }^{\circ}\text{C}$ to $>2000\text{ }^{\circ}\text{C}$) where sensor drift can be $>50\text{ }^{\circ}\text{C}$ over a period of a few tens of hours.

Currently, the only reported use of metal-carbon eutectic fixed-points for self-validation of thermocouples is that of Pearce et al. [16, 18, 19]. They employed the design of Tischler [7, 20] *et al.* where the fixed-point comprises the measurement junction; a bare-wire platinum-rhodium thermocouple was used. Excellent repeatability was found with the Co-C fixed-point which clearly demonstrates the feasibility of the concept and hold out great promise for extension of the principle of self-validation to higher temperatures with W-Re thermocouples.

2.2 OBJECTIVES

The project aimed to design both a single-cell and a multi-cell HTFP, to construct both designs with a series of ingots, and to thoroughly test these HTFPs at high temperature. The testing consisted of thermal cycling and endurance tests. A functional breadboard to allow further use of the self-validating thermocouples was also to be provided.

The design requirements are as follows:

- Different concepts shall be taken into consideration including one for the single cell thermocouples and one for the multiple cell thermocouples.
- The preliminary design shall be produced for single cell thermocouples and multiple cell thermocouples. The design shall be made for different carbon eutectic temperature plateaus:
 - $1324\text{ }^{\circ}\text{C}$ (Co-C)
 - $1738\text{ }^{\circ}\text{C}$ (Pt-C)
 - $1953\text{ }^{\circ}\text{C}$ (Ru-C)
 - $2292\text{ }^{\circ}\text{C}$ (Ir-C)
- The multiple cell thermocouples shall be divided into one for lower temperature range (i.e. Co-C and Pt-C) and one for higher temperature range (i.e. Pt-C and Ru-C).
- The system shall take into account:
 - Material compatibility of the thermocouple type, insulator material, sheath material, crucible material, and metal-carbon eutectic at the given temperatures
 - Influence of material contamination on the melting point of the metal-carbon eutectics
 - The ageing effects at different maximum temperatures
 - Thermocouples and overall system shall be as small as possible.

Some differences between the requirements outlined here and those stated in the Project Statement of Work exist, and this is discussed within Project Technical Notes.

It was agreed that in the event of mechanical/structural/operational failure of the self-validating sensor assembly, post-test material examination would include the following:

- Analysis of the thermo-mechanical situation of the various thermocouple systems
- Appropriate optical and electro-optical microscopic examinations of the thermocouples and fixed-points, such as energy dispersed X-ray fluorescence (EDX), electron probe micro analysis (EPMA), and/or other appropriate techniques.

2.3 TECHNICAL METHOD

2.3.1 Self-validating thermocouples; design and manufacture

The design of the self-validating thermocouples is based on HTFP ingots. Each ingot is contained in a cylindrical graphite crucible with the outer dimensions: 14 mm diameter, 30 mm length. To form the self-validating thermocouple, each are placed on the tip of a W-Re Type C thermocouple. The thermocouples used for this project were supplied by Omega Engineering, UK with a customised design to ensure good thermal immersion of the measuring junction into the HTFP cells. The thermocouples have a tantalum sheath with an outer diameter of 7 mm. This arrangement is shown, with the Swagelok adaptor in place (which provides the gas-tight seal to the furnace), in Figure 1.

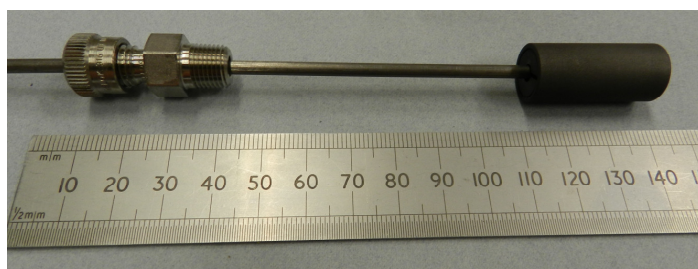


Figure 1: The self-validating thermocouple arrangement, showing the Swagelok adaptor fitted to the Type C thermocouple, and HTFP cell positioned on the thermocouple tip.

Six cells were constructed and tested. Four of these contained a single fixed-point ingot (the *single-cells*), and two of these contained two fixed-point ingots (the *multi-cells*). These are listed:

Single-cells:	Co-C (~1324 °C), Pt-C (~1738 °C), Ru-C (~1953 °C) and Ir-C (~2289 °C) ¹
Multi-cells:	Co-C & Pt-C, and Pt-C & Ru-C

During thermal cycling, several of the crucible walls were observed to show hairline cracks. Figure 2 shows an example. As the metal-carbon ingots were **at all times** fully contained within the graphite crucibles, it was decided that these did not constitute significant damage.

¹ Note the temperatures quoted here are those nominally measured



Figure 2: Ru-C single-cell, after thermal cycling.

The only exception was for the Co-C & Pt-C multi-cell. During the first test after construction, it was found that this cell was not robust enough to contain the Co-C ingot. Post-test analysis methods were employed and it has been concluded that this extreme case was due to extensive erosion of the graphite wall around the Co-C ingot. This may be because of the relatively high temperature exposure of the ingot (when the Co-C ingot is exposed to temperatures high enough to melt the Pt-C ingot, it is $\sim 414\text{ }^{\circ}\text{C}$ above its own melting temperature). No measurement results for this cell will be reported here. Further details are available in the Project Technical Notes.

2.3.2 Traceable temperature assignment to HTFP cells

Radiation thermometry was used to measure the melting temperature of each of the single-cells both before and after the test measurements; and after tests on the Pt-C & Ru-C multi-cell. This was completed according to ISO 17025 accredited procedures and results in a melting temperature and uncertainty traceable to NPL's realisation of the International Temperature Scale of 1990 (ITS-90). This allows for any drift in the HTFP cell melting temperature to be observed.

2.3.3 Self-validating thermocouples: testing

The testing procedure consists of two parts: thermal cycling and endurance. For the first, the self-validating thermocouples were exposed to five thermal cycles through their melt and freezing temperature/s – in each case returning to room temperature before the next cycle. For the second, the self-validating thermocouples were exposed to a temperature approximately $50\text{ }^{\circ}\text{C}$ above the (highest) melting temperature and held in this environment for 10 h.

2.3.4 Breadboard

The arrangement used at NPL to perform these tests is shown in Figure 3. The breadboard, to implement the self-validating thermocouples, has been delivered to ESA-estec (Noordwijk). The details are available in the Project User Manual.

Note in the furnace used by NPL the furnace temperatures below $1500\text{ }^{\circ}\text{C}$ are set by using an independent Type C thermocouple, and those above $1500\text{ }^{\circ}\text{C}$ with a pyrometer.



Figure 3: The breadboard as arranged at NPL.

2.4 TEST RESULTS & OUTCOMES

2.4.1 Traceable temperature assignment to HTFP cells

Radiation thermometry was used to measure the melting temperature of each of the single-cells both before and after the test measurements; and after tests on the Pt-C & Ru-C multi-cell. This was completed according to ISO 17025 accredited procedures and results in a melting temperature and uncertainty traceable to NPL's realisation of the International Temperature Scale of 1990 (ITS-90). These measured temperatures and the associated uncertainties are given in Table 2. Typical radiation thermometry measurements of the plateaus are shown in Figure 4.

All units °C	Single-cells				Multi-cell	
	Co-C	Pt-C	Ru-C	Ir-C	Pt-C	Ru-C
Before tests						
Melting temperature	1323.43	1737.71	1952.87	2289.71	--	--
Uncertainty ($k = 2$)	0.64	0.94	1.00	1.56	--	--
After tests						
Melting temperature	1323.73	1737.53	1952.80	2289.76	1739.36	1955.58
Uncertainty ($k = 2$)	0.33	0.86	1.03	1.60	1.19	1.88
After tests						
Drift (after-before)	0.30	-0.18	-0.07	0.05	--	--

Table 2: Melting temperature and uncertainty of the HTFP cells calibrated (before and after tests were performed). Uncertainties are expressed in terms of a 95% confidence level, coverage factor $k = 2$.

The radiation thermometry measurements after the tests were performed show that the melting temperature of the HTFP cells has not drifted significantly with use. The melting temperature assigned and the difference between this value (after tests) from the initial value (before tests) is given in Table 2. The difference found, lies well within the uncertainty of the temperature assignment and is largest for the Co-C single cell (0.30 °C) and smallest for the Ir-C cell (0.05 °C). The melting temperatures assigned to each of the ingots within the multi-cell are significantly higher (~2 °C), as were the uncertainties, than those assigned to the single-cells. This indicates that the thermowell is not so well isolated from the external furnace temperature: in this cell design only half of the thermowell length is in contact with the melting ingot at any time, the other half (containing the alternative ingot) is shown to respond to the changing temperature of the furnace.

The HTFP melting temperature is determined from the point of inflection by fitting a third-order polynomial function. Also note that the output (emf) of the self-validating thermocouple at the freezing temperature of the fixed-point is defined to be the maximum emf reached after the super-cool (that occurs prior to nucleation) and subsequent freezing.

2.4.2 System calibration

A system calibration was performed to demonstrate the proof of concept, using the Co-C (1324 °C) and Pt-C (1738 °C) HTFPs.

The HTFP cells were mounted on Type C thermocouples, and the melting and freezing curves measured. These are shown in Figure 5. As can be seen there is a hesitation (or plateau) in the thermovoltage at the melting temperatures of the Co-C and Pt-C point. When the self-validating sensors were used in practice these features would be used to calibrate *in-situ* the thermocouple output.

It can be seen in the figure that the plateau measured with the Co-C and the Pt-C HTFP cells, for these initial measurements, have a different shape. This is ascribed to differences in the thermocouple manufacture and therefore the immersion depth of the measurement junction into the HTFP cell.

These measurements represent the functional testing of the equipment; see Table 3 for itemisation. In addition, as the melting temperatures have been determined by radiation thermometry (see Section 2.4.1) this measurement represents a system calibration.

Action	Pass/fail
DVM operational	Pass
Automatic reference junction operational	Pass
PC operational	Pass
GPIB interface operational	Pass
Logging software operational (logging DVM output)	Pass
Thermocouple detects melt/freeze plateau	Pass

Table 3: Functional testing objectives and pass/fail result.

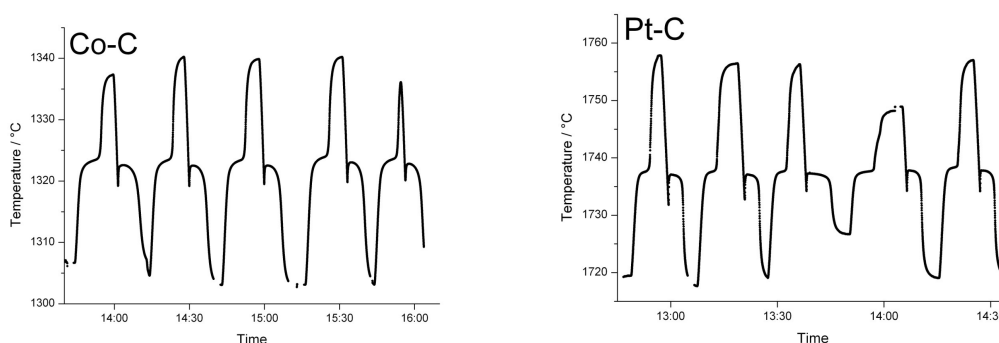


Figure 4: Radiation thermometer measurements of the Co-C (left) and Pt-C (right) HTFP cells.

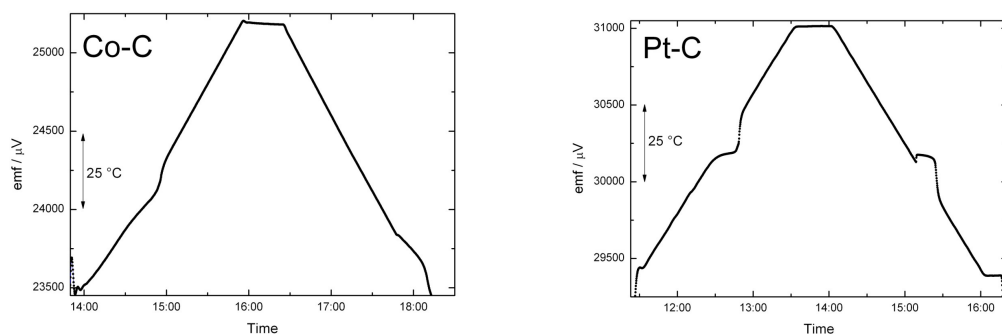


Figure 5: Thermocouple measurements of the Co-C (left) and Pt-C (right) HTFP cells.

2.4.3 Thermal cycling of single-cells

Each self-validating thermocouple was subjected to five thermal cycles, which melted and froze the HTFP ingot from room temperature, once per cycle. The controlled furnace conditions are given in Table 4, for each of the self-validating thermocouples. The settings vary due to practical reasons; at 1500 °C, the high temperature furnace used at NPL for these tests switches between thermocouple and pyrometer control (so a dwell was used at 1500 °C, to ensure this occurs correctly). A dwell was also set (at approximately 50 °C above and below the fixed-point transition temperature) to allow the furnace and its contents to reach thermal equilibrium.

	Co-C	Pt-C	Ru-C	Ir-C
Ramp	20 °C / min	20 °C / min	20 °C / min	20 °C / min
Dwell	1255 °C (for 5 min)	1500 °C (for 5 min)	1500 °C (for 5 min) (a)	1500 °C (for 5 min)
Ramp	1 °C / min	10 °C / min	10 °C / min	10 °C / min
Dwell	1355 °C (for 100 min)	1700 °C (for 5 min)	1900 °C (for 5 min) (b)	2000 °C (for 5 min)
Ramp	1 °C / min	1 °C / min	1 °C / min	3 °C / min
Dwell	1255 °C (for 15 min)	1770 °C (for 100 min)	2000 °C (for 100 min)(c)	2200 °C (for 5 min)
Ramp	--	1 °C / min	1 °C / min	1 °C / min
Dwell	--	1700 °C (for 15 min)	1900 °C (for 15 min) (d)	2300 °C (for 100 min)
Ramp	--	--	--	1 °C / min
Dwell	--	--	--	2200 °C (for 15 min)

Table 4: Test program for the thermal cycling of self-validating thermocouples with each single-cell. The Ru-C program is shown in Figure 6 where the dwells marked a-d are also shaded.

As an example, the furnace set-point conditions for the Ru-C single-cell are shown by the dark yellow line in Figure 6. In the same figure, a measured melt and freeze of the Ru-C cell is shown (black line) – where the melt and freeze plateaus are identified in red ovals.

Initially a fast ramp rate is used, to quickly reach the temperature region of interest. At low temperatures, the furnace is controlled by a Type C thermocouple, but at 1500 °C this control switches to a pyrometer – requiring a pause in the ramp conditions (at 1500 °C), to allow the system to complete this switch-over. This pause is shown in Figure 6 as shaded region (a).

Approximately 50 °C lower than the ingot melting temperature, the program is again paused (shaded region (b)), and the ramp rate is changed to a condition suitable for observing the phase transitions of these HTFP cells. In this case, a rate of 1 °C/min is found to be suitable – providing a clear plateau with a duration of ~15 min for both the melt and freeze transitions. If the furnace is required to go above 2000 °C, a further pause is included in the program, to allow the system to stabilise before ramping to higher temperatures (in the high temperature furnace NPL used, this is found to be

necessary, but may not be the case for other furnaces). The program is then set to dwell at the maximum temperature for 1 h (shaded region (c)) – before cooling through the ingot freeze. A further dwell at a temperature $\sim 50^\circ\text{C}$ below the freeze is then set (shaded region (d)), before switching off the heaters and allowing the system to cool down naturally.

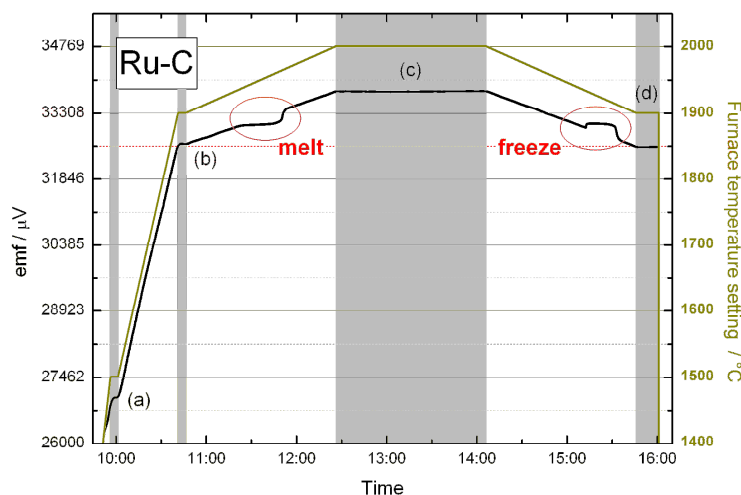


Figure 6: An example measurement of the melt and freeze of the Ru-C single-cell (black line, left axis). The dark yellow line (right axis) shows the controlled furnace set-point temperature. The red ovals indicate the melt and freeze transition plateaus and the shaded areas show the furnace dwell steps (a-d).

Five cycles of each single-cell were measured. The results of each are shown in Figures 7 and 8. The measurements shown were all collected in the same order – with the black curve first, followed by the red, green, dark blue and light blue curves. The same Type C thermocouple was used for all the measurements in each series. The sensitivity of the Type C thermocouple at these temperatures is indicated in the figures; $\sim 14\ \mu\text{V}/^\circ\text{C}$ at Co-C, $\sim 14\ \mu\text{V}/^\circ\text{C}$ at Pt-C, $\sim 12\ \mu\text{V}/^\circ\text{C}$ at Ru-C and $\sim 8\ \mu\text{V}/^\circ\text{C}$ at Ir-C. These show clear melting and freezing plateaus for each self-validating thermocouple, with some differences in the length and shape of the plateaus between Co-C, Pt-C and Ru-C measurements.

The plateau length is typically observed to be 15 minutes long in this test, which indicates that a faster ramp rate should also be suitable for observing the plateau – which would be typical in industry and result in a shortened plateau duration. However a plateau shorter than 10 minutes should be treated with some caution when determining the inflection temperature, particularly if the thermocouple output becomes noisy. If the plateau is unclear with a new thermocouple, this may be due to differences incorporated during thermocouple manufacture which lead to slightly different immersion depths of the measuring junction for each thermocouple – this effect is illustrated in Figure 9. These results show that these self-validating thermocouples are suitable for providing repeatable measurements under the conditions used here.

The thermocouple at the highest temperature fixed-point (the Ir-C point, Figure 8) is clearly very unstable. This is typical behaviour for W-Re thermocouples under these conditions and therefore shows the thermocouple would be unreliable in use without the HTFP cell for validation. This temperature is at the upper limit of the manufacturers recommended exposure range for this type of thermocouple. For each measurement of this point, the melting and freezing plateaus are often difficult to identify. By plotting the five measurements on a single graph and shifting the measurements in time to overlay the furnace conditions, it becomes clear that the phase transitions occur at the same point during the program.

The output (emf) of the self-validating thermocouples at the HTFP melt and freeze points have been calculated and are shown in Figure 10.

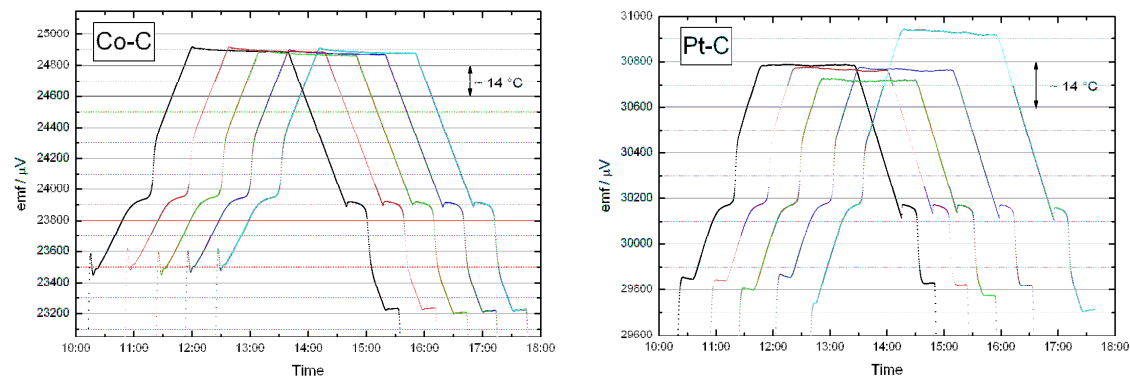


Figure 7: Left – Five melt and freeze cycle measurements of Co-C single-cell. Right – Five melt and freeze cycle measurements of Pt-C single-cell (note, the maximum furnace set point for the Pt-C light blue curve was set to 1790 °C, not the stated 1770 °C).

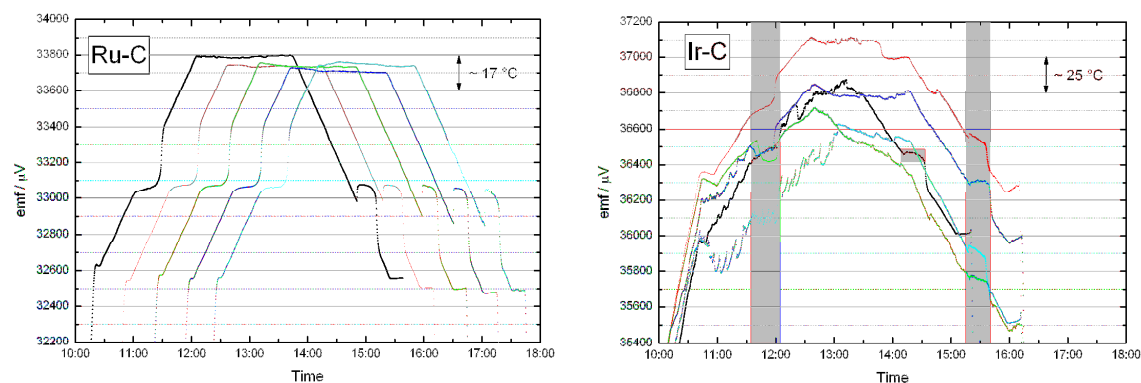


Figure 8: Left – Five melt and freeze cycle measurements of Ru-C single-cell. Right – Five melt and freeze cycle measurements of Ir-C single-cell, shaded areas indicate melt and freeze regions (note, the dwell time for the Ir-C black curve was set to 1 h, where the others are 1 h 40 m).

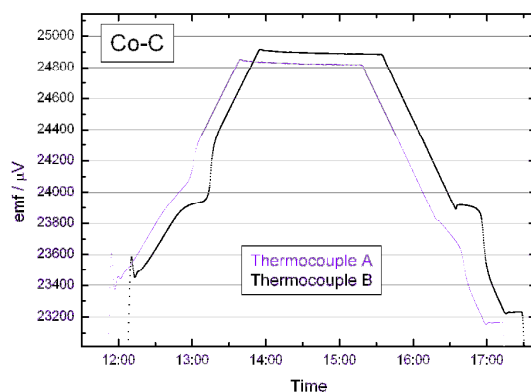


Figure 9: A comparison of measurements taken with a Type C thermocouple, in the Co-C single-cell, with good immersion (black) and poor immersion (purple).

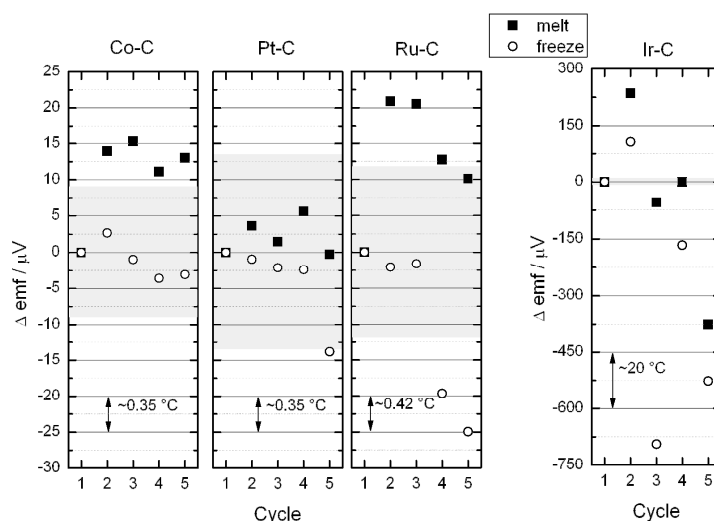


Figure 10: The measured emf at the melt and freeze transitions of the single-cell self-validating thermocouples (difference from first measurement). Shaded areas indicate HTFP temperature assignment uncertainty (as determined by radiation thermometry as described in Section 2.4.1).

For example, the first two melting transitions of the Ru-C self-validating thermocouple are found to lie 20.9 μV apart – which corresponds to a drift of $\sim 1.7^\circ\text{C}$, which is larger than the temperature assignment uncertainty of the HTFP. It is therefore clear that a correction which could be performed due to the presence of the HTFP cell would be necessary to maintain optimum operation of the thermocouple.

2.4.4 Thermal endurance of single-cells

The procedure used for the endurance test of the single-cells is the same as given in Table 4, with the dwell time at the maximum temperature increased to 10 h. Each self-validating thermocouple was exposed to this procedure once and the measurements are shown in Figure 11 – where the thermocouple emf measured is plotted vs. time (the curves have been shifted vertically for display and hence the quantitative scale removed; each major grid line indicates 500 μV).

The extent of the drift of the thermocouple in-use can be quantified by considering the emf change over the time at the maximum temperature (10 h dwell). At the start of the 10 h dwell, typically 15 minutes are required before the temperature is stable (some furnace overshoot of the required temperature occurs due to the previous ramping command). In addition, some time is required for the furnace and HTFP cell to reach thermal equilibrium at the set temperature – therefore the changing measurement in the first 30 minutes is not due solely to the thermocouple drift. The difference between the thermovoltage measured after 5 h and 10 h (i.e. the second half of the 10 h dwell), for the three lower temperature self-validating thermocouples (Co-C, Pt-C and Ru-C) show a drift of less than 1°C . However the Ir-C self-validating thermocouple was observed to drift by $\sim 43^\circ\text{C}$ over these five hours and the measured difference between the melt and freeze plateaus is also large ($\sim 88^\circ\text{C}$), confirming the extent of the drift and enabling the user to correct the thermocouple output for drift, with confidence.

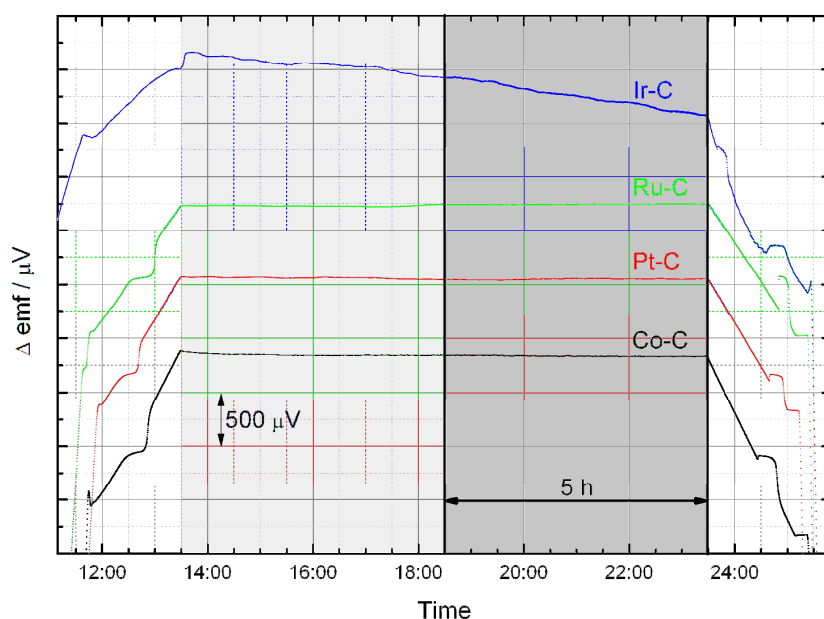


Figure 11: A single endurance measurement of each single-cell (note that the lines have been shifted vertically for display). Note the large drift in the Ir-C output over the duration of the test.

2.4.5 Thermal cycling of multi-cell (Pt-C & Ru-C)

The details of the temperature cycle used for the Pt-C & Ru-C multi-cell are given in Table 5. The Pt-C & Ru-C multi-cell was successfully measured through five melt and freeze cycles. These are shown in Figure 12 (Left). Both the Pt-C and Ru-C transitions are clearly observed – with a typical melting plateau length of just over 10 minutes. This duration is shorter when compared to the single-cells because of the reduced mass of the ingot. The results for each transition are plotted in Figure 12 (Right).

	Pt-C & Ru-C multi-cell	
	Pt-C	Ru-C
Ramp	20 °C / min	
Dwell	1500 °C (for 5 min)	
Ramp	10 °C / min	
Dwell	1700 °C (for 5 min)	
Ramp	1 °C / min	
Dwell	1790 °C (for 15 min)	
Ramp	→	5 °C / min
Dwell		1900 °C (for 5 min)
Ramp		1 °C / min
Dwell		2000 °C (for 15 min)
Ramp		1 °C / min
Dwell		1900 °C (for 15 min)
Ramp		5 °C / min
Dwell		1790 °C (for 5 min)
Ramp	1 °C / min	←
Dwell	1700 °C (for 15 min)	

Table 5: Test procedure for thermal cycling of the Pt-C & Ru-C multi-cell

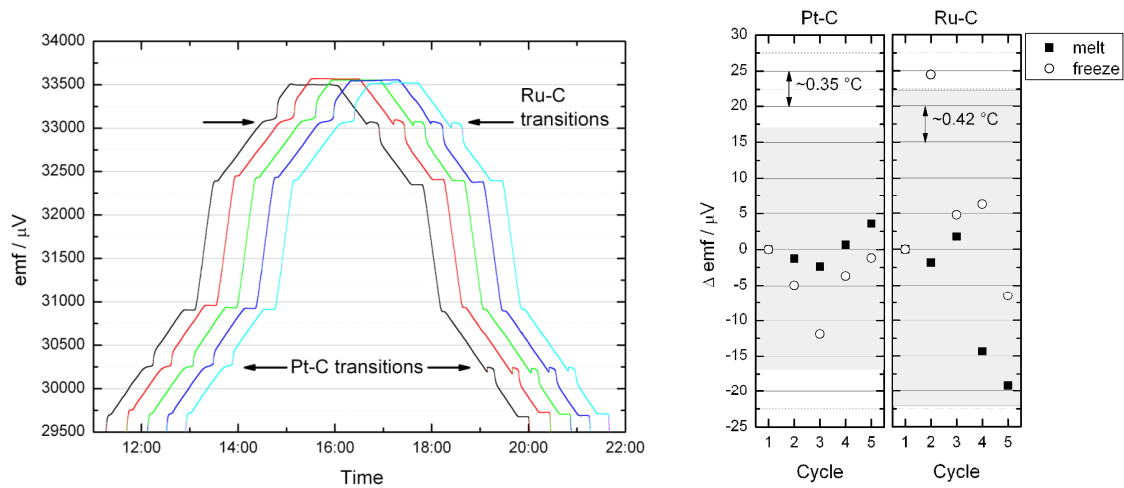


Figure 12: (Left) Five melt and freeze cycle measurements of Pt-C & Ru-C multi-cell. (Right) The measured emf at the melt and freeze cycle transitions of the Pt-C & Ru-C multi-cell self-validating thermocouple. Shaded areas indicate temperature assignment uncertainty of the HTFP (as determined after the thermocouple measurements).

2.4.6 Thermal endurance of multi-cell (Pt-C & Ru-C)

The Pt-C & Ru-C self-validating thermocouple was exposed to the endurance test once. The procedure used to measure the temperature endurance cycle is as given in Table 4, but with the dwell time at the maximum temperature increased to 10 h. The measurement result is shown in Figure 13. The difference in the thermocouple output at the melting and freezing plateaus of the two HTFPs is ~ 0.9 °C for both the Pt-C and the Ru-C.

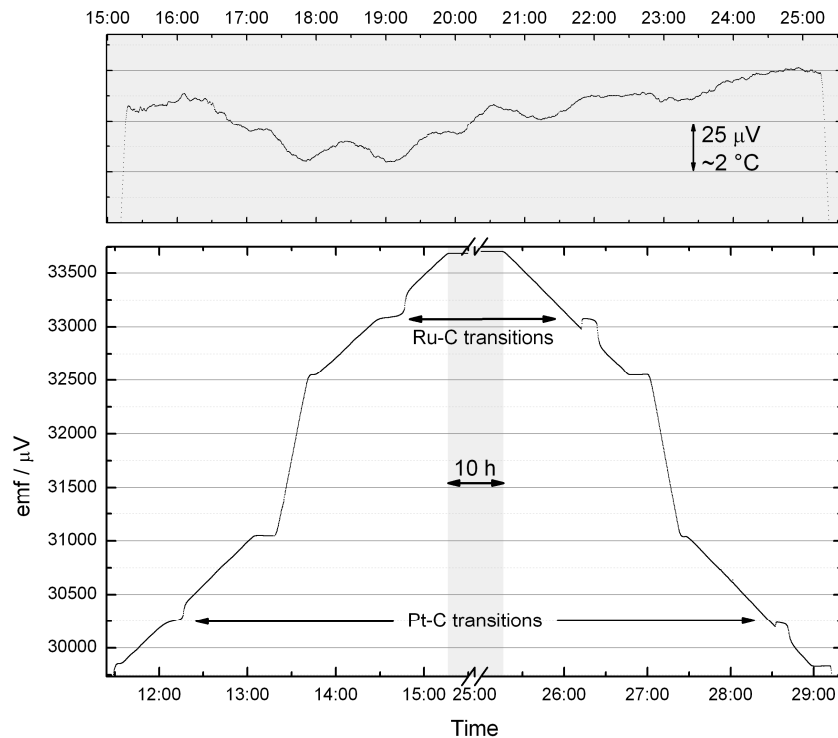


Figure 13: Lower – The endurance measurement of the Pt-C & Ru-C multi-cell. Upper – Shows only the thermovoltage during the 10 h dwell at 2000 °C.

The drift observed in the thermovoltage in the last 5 h of the endurance test (at the holding temperature of 2000 °C is -23.69 μV (~ 2 °C upwards). Although this is the measure used above for the single-cell endurance tests, it is not directly applicable here since the thermocouple is seen to drift both up and down over this endurance test – as shown in the upper panel of Figure 13.

2.5 PROCEDURE FOR IMPLEMENTING DRIFT CORRECTION

There is a simple procedure which can be followed to implement the self-validating thermocouple. The four steps for implementation are given here, with some discussion:

- Install the self-validating thermocouple. In the current design, the cell should be installed from within the furnace (access through the same port and pathway as the thermocouple may not be possible).
- Proceed with routine temperature process. The self-validating thermocouple may be used to control the furnace temperature, but the user should be aware that for the duration of the melt and freeze transitions, the furnace should be controlled independently of the self-validating thermocouple (since it will not be reflecting the furnace temperature during these times). At temperatures cooler than the HTFP transition temperature, the HTFP cell is known to be robust at heating rates of up to 20 °C/min.
- Observe and measure the HTFP transition temperature. The user should record the thermocouple measurements throughout the phase transition plateau, and fit a third order polynomial (as provided in the breadboard; “Best Fit” software) to determine the thermocouple reading (emf) at the melting temperature of the HTFP cell. Some considerations are mentioned below*.
- Correct the temperature conversion algorithm. The algorithm used to convert thermocouple output to temperature may then be corrected immediately (i.e. during operation) or retrospectively (i.e. during post-process analysis). This is described in more detail below**.

* Observing the plateau depends on suitable thermocouple immersion, and also on the temperature around the HTFP cell during the transition. The furnace temperature, whilst the transition is observed, may be continually increasing (as in the tests described here) or it may dwell at a set temperature (above the melting temperature, for example). In either case, the duration of the plateau observed will depend on the extent of these temperature conditions. In the tests described here, a typical plateau duration of ~ 15 mins is observed. This could be increased by decreasing the furnace ramp rate (or the difference between the melting temperature and the furnace dwell temperature); alternatively it could be decreased by increasing the settings. It is important to note that a particularly short plateau duration will not provide enough information for the user to determine the melting temperature with a suitable level of confidence. It is recommended that a plateau shorter than 10 mins, be treated with some caution. Further cycles of the self-validating thermocouples would be needed to determine ramp rate conditions for achieving different plateau lengths.

** There are several methods which can be envisaged to correct for thermocouple drift using a self-validating thermocouple. These would be suitable for different applications and depend on the user’s temperature range of importance and the tolerance required. Some examples follow:

- If, for instance, the user is operating over a small range, at around 2300 °C, and cycling through the Ir-C transition temperature periodically during the process; it is shown that the thermocouple will display ~ 40 °C of drift over 5 h. In this case the user may wish to immediately adjust the interpretation of temperature linearly across the range by the amount determined by the HTFP cell measurement, and maintain that new setting until the next HTFP measurement. The accuracy of this method is reasonable, since the drift is extreme. Over time, the user may observe a pattern; in which case the user will be empowered to apply a correction in smaller graduations, and verify this at the next HTFP measurement.
- If, for example, the user is operating over a wide range, and at a lower temperature (where the thermocouple drift is less severe), the appropriateness of a single-cell is limited, since the drift

at a temperature far from the HTFP transition temperature may bear little or no resemblance to that recorded at the HTFP transition temperature. In this case, the multi-cell should be employed and the drift at two temperatures (preferably above and below the region of interest) should be recorded. This information can be used to give confidence that the temperature measurements at these two places remains within the expected uncertainty, and it can therefore be implied that the measurement over the range between the two is not drifting. Any small drifts observed may be adjusted for immediately. If the drifts in the HTFP measurements (above and below the region of interest) are particularly different from one another, it is recommended that a linear extrapolation between the two should be applied for the range in question.

2.6 CONCLUSIONS

The design, construction and testing of self-validating thermocouples has been successfully completed. In particular, the miniaturisation of HTFPs (to a level where *in-situ* measurements can be made) has been shown to be possible, while still providing suitable immersion for clear HTFP transition observation.

The self-validating thermocouples based upon the following HTFPs were constructed:

Single-cells: Co-C (~1324 °C), Pt-C (~1738 °C), Ru-C (~1953 °C) and Ir-C (~2289 °C)
Multi-cells: Co-C & Pt-C, and Pt-C & Ru-C

During construction, it was found that some of the cells showed hairline cracks on the outside of the graphite crucible. Construction and tests continued, and the cracks did not become significant enough to cause any operational issues. The exception was the Co-C & Pt-C multi-cell which was not robust enough to withstand the tests. This was investigated and found to be due to severe erosion of the graphite walls. Until further investigations can be made, it is recommended that the temperature difference between the HTFP pair within a multi-cell should be kept to a minimum.

Thermal cycling of the single-cells was completed successfully and the thermocouple output at the resulting melt and freeze plateaus were calculated and plotted, to clearly show that these (even after a single cycle) may fall outside of the original validation uncertainty. Thermal endurance of these cells showed that the Ir-C self-validating thermocouple was severely affected, drifting by ~88 °C over 10 h exposure.

Thermal cycling and an endurance test of the multi-cell Pt-C & Ru-C were completed successfully – the reduced ingot size did not impair the observation of the melting and freezing plateaus.

A melting temperature and uncertainty, traceable to NPL's realisation of the International Temperature Scale of 1990 (ITS-90) have been determined for the HTFP cells. This was completed for all the single-cells, both before and after the thermal tests. This showed no significant change in the cell performance – and therefore all drifts observed during the thermal tests were due to the thermocouple and can be corrected for with confidence.

Traceable temperatures were also assigned to the Pt-C & Ru-C multi-cell after the thermal tests were complete. These showed an increase in the assigned temperature, and uncertainty, (when compared to the equivalent single cells) of ~2 °C. This indicates that the thermowell is not so well isolated from the external furnace temperature: in this cell design only half of the thermowell length is in contact with the melting ingot at any time, the other half (containing the alternative ingot) is shown to respond to the changing temperature of the furnace.

The four stages of a simple user procedure for implementing thermocouple drift correction are given and two examples of different scenarios are discussed. The single-cells are suitable for monitoring and

correcting the drift over a narrow temperature range, whereas the multi-cells (where the HTFP temperatures are chosen to be above and below the range of interest) are suitable for monitoring and correcting the drift over a wide temperature range.

In summary the designs developed within this project are successful – these measurements have shown that Type C (W-Re) thermocouples drift significantly at high temperatures, even over the short time periods used here (1 h – 10 h) and that this design of self-validating thermocouple is suitable for such *in-situ* observation. Self-validation is therefore necessary for continuing confidence in W-Re thermocouple measurements above 1300 °C.

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4 REFERENCES

1. G. Machin, “Realising the benefits in improvements in high temperature measurement”, *Acta Metrologica Sinica* **29**, 10-17 (2008)
2. Y. Yamada, H. Sakate, F. Sakuma and A. Ono, “High temperature fixed points in the range 1150 °C to 2500 °C using metal-carbon eutectics”, *Metrologia*, **38**, 213-219 (2001)
3. E. Woolliams, G. Machin, D. Lowe and R. Winkler, “Metal (carbide)-carbon eutectics for thermometry and radiometry: a review of the first seven years”, *Metrologia*, **43**(6), R11-R25 (2006)
4. G. Machin, “Improvements in high temperature metrology”, *Measure*, **3**, 36-42 (2008)
5. K. Anhalt, J. Hartmann, D. Lowe, G. Machin, M. Sadli, Y. Yamada and P. Bloembergen, “A comparison of Co-C, Pd-C, Pt-C, Ru-C and Re-C eutectic fixed-points independently manufactured by three different institutes”, *Proc. Newrad (Davos)*, Ed. J. Groebner, 289-290 (2005)
6. K. Anhalt, J. Hartmann, D. Lowe, G. Machin, M. Sadli and Y. Yamada, “Thermodynamic temperature determinations of Co-C, Pd-C, Pt-C and Ru-C”, *Metrologia*, **43**(2), S78-S83 (2006)
7. M. Tischler and C. Anteneodo “Thermoelectric fixed point thermometer”, *Temperature Measurement*, China Academic Publishers (Beijing), 192-197 (1982)
8. R. Morice, F. Edler, J. Pearce, G. Machin, J. Fischer and J-R. Filtz, “High-temperature fixed-point facilities for improved thermocouple validation – Euromet project 857”, *Int. J. Thermophys.*, **29**(1), 231-240 (2008)

9. F. Edler and A.C. Baratto, "A cobalt-carbon eutectic fixed point for the validation of contact thermometers at temperatures above 1100 °C", *Metrologia*, **42**(4), 201-207 (2005)
10. H. Ogura, M. Izuchi and M. Arai, "Evaluation of cobalt-carbon and palladium-carbon eutectic point cells for thermocouple validation", *Int. J. Thermophys.*, **29**(1), 210-221 (2008)
11. Y-G. Kim, I. Yang, S.Y. Kwon and K.S. Gam, "Features of Co-C and Ni/C eutectic transitions for use in thermocouple thermometry", *Metrologia*, **43**(1), 67-70 (2006)
12. J.V. Pearce, G. Machin, T. Ford and S. Wardle, "Optimising heat-treatment of gas turbine blades with a Co-C fixed-point for improved in-service thermocouples", *Int. J. Thermophys.*, **29**(1), 222-230 (2008)
13. J.V. Pearce and G. Machin, "A robust Pd-C fixed point for validation of thermocouples", *Acta Metrologica Sinica*, **29**, 224 (2009)
14. J.V. Pearce, V. Montag, D. Lowe and W. Dong, "Melting temperature of high temperature fixed points for thermocouples validations", *Int. J. Thermophys.* (in press) (2010)
15. R. Morice, P. Ridoux and J.R. Filtz, "Improved measurements in contact thermometry at high temperatures through practical fixed points", *Measure* **3**(1), 44-49 (2008)
16. J.V. Pearce, O. Ongrai, G. Machin and S. Sweeney, "Self-validating thermocouples based on high temperature fixed points", *Metrologia*, **47**(1), L1-L3 (2010)
17. R. Morice, M. Megharfi, J-O. Favreau, E. Morel, I. Didialaoui and J-R. Filtz, "Realisation of metal-carbon fixed-points for validation of contact thermometers at high temperatures", *Proc. Tempmeko 2004*, , Zagreb, Croatia, Ed. Davor Zvizdic, LPM/FSB, 847-852 (2005)
18. J. Pearce, O. Ongrai, and G. Machin, "NPL developing self-validating thermocouples based on metal-carbon eutectic fixed points", *Measure*, **4**, 5 (2009)
19. O. Ongrai, J.V. Pearce, G. Machin and S.J. Sweeney, "Miniature Co-C eutectic fixed point cells for self-validating thermocouples", *Meas. Sci. Tech.*, **22**, 015104 (2011)
20. M. Tischler and M.J. Koremblit "Miniature thermoelectric fixed points for thermocouple validation", *Temperature: Its Measurement and Control in Science and Industry*, **5**, 383-390 (1982)