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Manufacturing of MC Eutectics and Reproducibility of Pt-C Eutectic Fixed Points using a Thermogauge Furnace

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Abstract National Institute of Metrology (NIM) (China) and National Physical Laboratory (NPL) (UK) have collaborated to construct metal-carbon eutectic alloy fixed points at NPL. A modified NPL Thermogauge furnace was vertically used to construct fixed points of Pd–C, Pt–C, Ru–C, and Ir–C. Breakage of Pd–C and Ru–C cells was traced to changes in furnace temperature gradients resulting from changing from horizontal to vertical operation. Subsequently, it was found that positioning the cell being filled so that the metal melting always starts from the top and freezing from the bottom to solve this problem. The constructed Pt–C cell was then compared to a Pt–C fixed point previously constructed by NIM. The results indicate that the two cells made independently agreed to be better than 40 mK.

Keywords Fixed point · High temperature · Metal-carbon eutectic alloy · Reproducibility

1 Introduction

The possibility of realizing high-temperature fixed points above the copper point using metal-carbon alloys was reported at TEMPMEKO ’99 [1]. Since then, metal-carbon eutectic fixed points have attracted a great deal of attention because of their inherent thermometric qualities [2–4].

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National Physical Laboratory (NPL) has been investigating metal-carbon eutectic fixed points since 1999. Eutectic fixed points based on cobalt, palladium, platinum, ruthenium, and rhenium were constructed using a horizontal furnace [5,6]. During comparison measurements, it was clear that improvements could be made to the melting curve [7,8]. One possible improvement was to modify the filling method to produce a uniform ingot without voids and porosity. In July to September of 2004, a set of eutectic fixed points was constructed using NPL-supplied materials with NMIJ facilities [8]. The good agreement found between these and the NMIJ cells confirmed the importance of the cell filling arrangement. The cell values agreed within 100 mK, the limit proposed for any high-temperature fixed point to be recognized as a primary fixed point [9]. NPL therefore decided to modify its filling procedure to use a vertical, rather than a horizontal, furnace to fill cells.

Platinum–carbon is likely to be one of the most important eutectic materials for a high-temperature fixed point if the proposed changes to the temperature scale realization and dissemination take place in the next 5 to 6 years [10]. NIM (China) and NPL (UK) have collaborated to construct a Pt–C fixed-point at NPL. This was then compared to a Pt–C fixed point previously constructed by NIM.

2 Filling of Fixed Points

Construction of the cells of Pd–C, Ru–C, Ir–C, and Pt–C was attempted using the new filling method. The filling furnace (Fig. 1) is a modified Thermogauge furnace with a

Fig. 1 Filling with the modified Thermogauge furnace

25.4 mm inner-diameter heater that can be used vertically. A graphite tube clamped between electrodes is used as a work tube and heater element. This is surrounded by graphite-felt insulation and a layer of graphite foil, all in a fused-silica tube. The whole assembly is enclosed by a water-cooled aluminum reflector. Argon purge gas floods the insulation around the heater; a second supply feeds argon directly into the work tube. The flow rates and vents are arranged so that gas flows outward from the work tube. The lower end of the work tube is blanked off with a graphite stopper. A window with a push-fit mount seals the top of the work tube. A pyrometer that used to monitor the melting process can view the furnace through the window. The cooling water has been arranged to flow from bottom to top as this can reduce the risk of air-locks. A 3 mm diameter graphite rod is fixed across the graphite tube heater to support the crucible (Fig. 4).

A separate heater/insulation/silica tube assembly was used for each fixed-point material to avoid cross-contamination. Before making a fixed point, first the empty furnace was heated to 100 °C above the temperature of use; then the empty crucible was baked for 30 min in argon.

In order to fabricate the cells, metal and graphite powders were weighed and mixed at 1% less than the eutectic composition. For the Pt–C cell, no graphite powder was added as the eutectic composition is only about 1%. Material was added to the crucible in an argon-filled glove-bag, and each filling melt was carried out under an argon atmosphere. After each fill and melt cycle, the fixed point was visually inspected. Any appearance of graphite on the surface was taken to be a sign of a hyper-eutectic alloy. Except for Pt–C, the carbon composition of the next fill could then be reduced by adding pure metal powder. Once the crucible was considered sufficiently full, the crucible end cap was screwed into place and the fixed point was considered complete. Details of the fixed points made are described in Table 1.

Initially during filling, the crucible was placed in the center of the furnace. Typical melting and freezing were done by manually increasing the power to give a heating rate of (20 to 30) °C · min^{-1} until the furnace was about (30 to 40) °C below the melt, waiting a short time, then increasing the power and observing the melting curve. After melting was completed, the power was adjusted to keep the crucible at about 40 °C above the eutectic temperature for 7 min; then the power was reduced. After freezing was finished, the power was adjusted to give a cooling rate of (20 to 30) °C · min^{-1}.

Three palladium, two ruthenium, one platinum, and one iridium cells were filled. The latter two Pd–C and one Ru–C cells broke during filling. The earlier Pd–C cracked after investigations were undertaken for examining the effect of the position of the fixed point within the realization furnace. The reason for the Ru–C breaking was that the

Table 1 Information concerning the fixed-point materials

	Graphite	Pd	Pt	Ru	Ir
Purity (%)	99.9999	99.999	99.999	>99.99	99.995
Source	Alfa Aesar	MV Lab	MV Lab	MV Lab	Alfa Aesar
Lot number	–	W605PDA1	W905PTA1	W705RUA1	IL02
Crucible	–	Tokai	Tokai	Tokai	Tokai

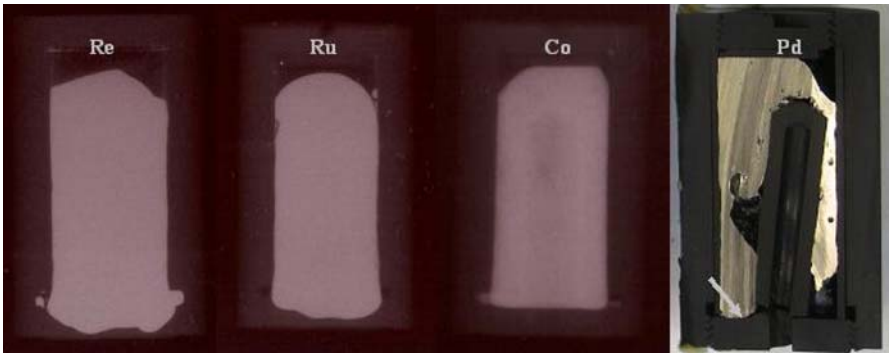

Fig. 2 X-ray photograph of the crucibles and a photograph of the sectioned Pd ingot

cell was incorrectly positioned during filling; it was 4 cm too high in the furnace tube. This suggested temperature non-uniformity of the furnace as a possible reason for the two Pd–C cells breaking. Another possible reason for the breakage is the slower melting/freezing, as a Pd–C cell with a higher melting/freezing speed had been filled successfully earlier. Another possible problem was incorrect filling; it can be seen in Fig. 2 that there are large voids in the Pd–C crucible that broke in use. It can also be seen that the graphite of the crucible bottom has been partly dissolved. X-rays were taken of other cells filled using the same arrangements, as shown in Fig. 2. All show that part of the graphite of the crucible bottom has dissolved. This was taken to be an indication that the temperature at the bottom of the crucible was probably too high.

3 Measurement of the Furnace Temperature Distribution

Previous work had shown agreement within <100 mK [11] between a rhenium cell made with these facilities and one prepared at NMIJ. Because of this, it had been assumed that the temperature uniformity was adequate and so no gradient measurements had been made. To remedy this, the distribution of the furnace temperature was determined by measuring the temperature of a graphite block inside the furnace using a pyrometer above the furnace. The graphite block could be moved up and down by a graphite rod of 6.35 mm diameter passing through a hole in the lower graphite end cap of the furnace. Measurements were made at the Pd–C, Pt–C, and Ir–C eutectic temperatures. The results are shown in Fig. 3, with dT the temperature difference between the block at position x and the geometric center of the furnace.

Subsequently, Pt–C and Ir–C cells were filled at a new crucible position (see Fig. 4). The crucible was put at a lower position than would be suggested from Fig. 3 to avoid melting starting from the bottom, where constrained expansion would be liable to cause the cell to rupture. X-ray investigation shows (Fig. 5) that good cells have been made, that is, the ingots are complete and the crucibles intact.

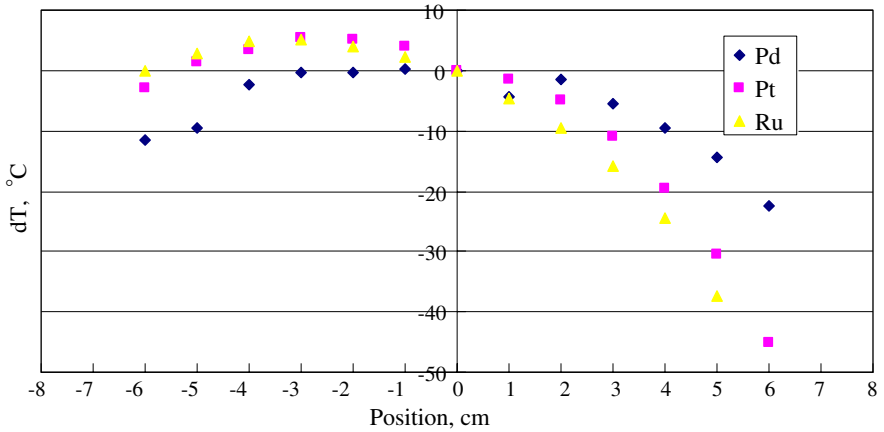

Fig. 3 Temperature distribution of the filling furnace

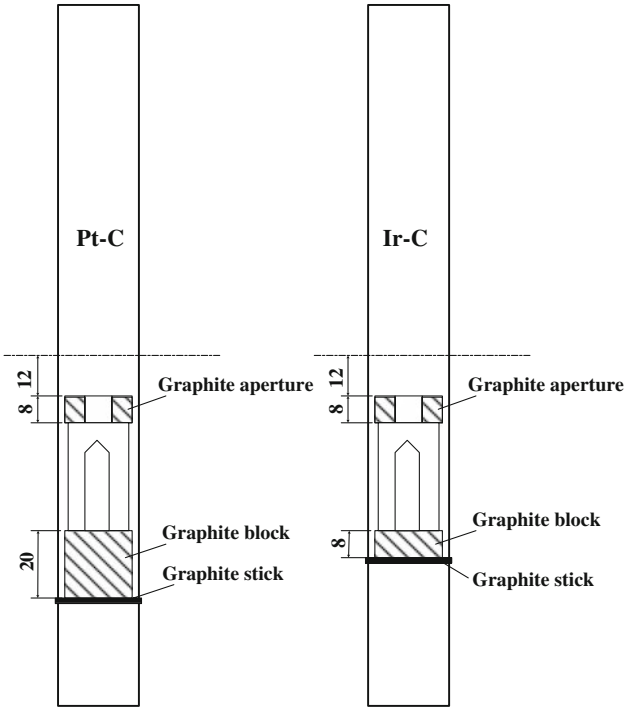

Fig. 4 Crucible arrangement for filling Pt–C and Ir–C. Dimensions are in millimeter

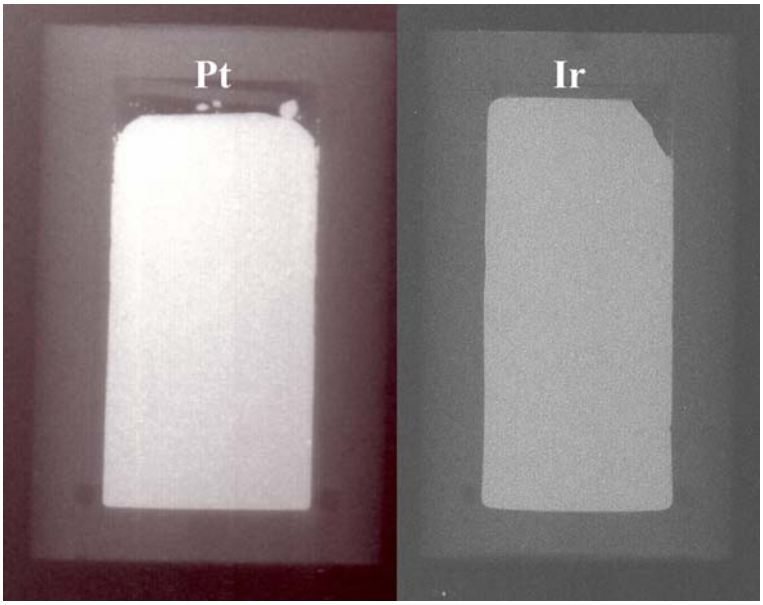

Fig. 5 X-ray photograph of the Pt–C and Ir–C

4 Comparison of the Pt–C Fixed Points

4.1 Description of the Pt–C Fixed Points

The cells of the NPL (200601) and NIM (NIM1#) have a similar design in size: outer diameter 24 mm; length 40 mm (NPL) and 45 mm (NIM); blackbody aperture 3 mm; blackbody depth 28 mm (NPL) and 34 mm (NIM); rear cone angle 120°; and isothermal emissivity >0.9996. The NPL cell was constructed with an inner graphite sleeve (Fig. 6a), and the NIM cell with an inner crucible lining made of three layers of

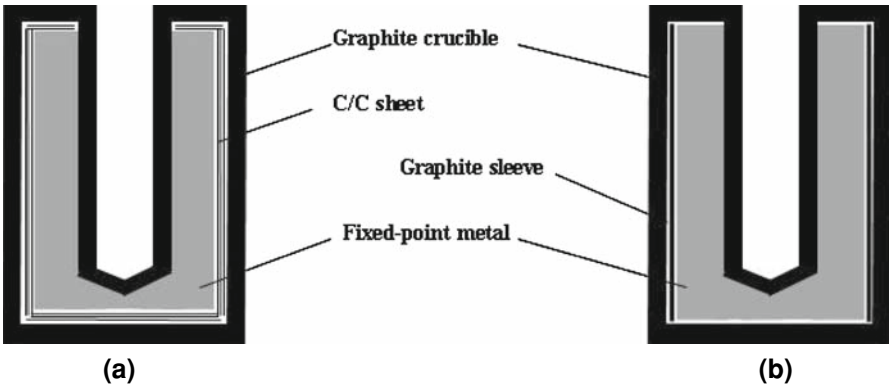

Fig. 6 Illustration of the difference in the inner crucible linings for the NIM and NPL fixed points

Table 2 Information concerning the NPL200601 Pt–C cell and NIM1#

Pt–C	Metal	Crucible	Graphite powder	Crucible lining	Metal mass (g)
NIM1#	Tanake/5N	SGL	Alfa Aesar/6N	C/C[a]	46
NPL200601	MV Lab/5N	Tokai	Alfa Aesar/6N	Graphite sleeve	69

[a] C/C: Flexible carbon-fiber composite (C/C) cloth

a flexible carbon-fiber composite (C/C) cloth (Fig. 6b), which acts as insulation and helps to remove effects due to furnace temperature gradients along the fixed point. Details of this technique and its advantages have been described in [12]. Table 2 gives information about the cells.

The Pt–C cell of NIM was constructed by NIM at NMIJ used a Nagano VR20-A10 filling furnace. This is a vertical furnace similar to the Nagano VR23-A10 [13]. The furnace was operated in vacuum when filling the Pt–C cell of NIM, in contrast to the NPL cell, which was filled in an argon atmosphere.

4.2 Comparison Measurement

A Thermogauge high-temperature furnace [14] was used for the comparison. This has a 25.4 mm inner graphite tube that is electrically heated. It operates without windows, the graphite components being protected from oxidation by argon at about $5\,\mathrm{L}\cdot\mathrm{min}^{-1}$ through a vent in the middle of the tube.

An LP3 pyrometer [15] was used for the temperature measurement, with a 650 nm central wavelength and a 10 nm bandwidth. The important quantity is the relative difference between cells. At the time of measurement, the LP3 had not been calibrated with NPL's temperature scale, so any absolute temperature values are for indication purposes only.

The crucibles were installed at the center of the furnace tube, graphite felt insulation of 20 mm thickness was put behind and in front of the crucible to improve the temperature uniformity in the furnace, and an aperture of 5 mm diameter was made in the front insulation to view the blackbody cavity. The distance between the LP3 and the aperture of the crucible was 830 mm.

Measurements alternated daily between the cells—3 days for the NIM cell and 2 days for the NPL cell. Generally, five sets of melt/freeze were recorded in one day for each cell. The furnace was heated to (20 or 10) °C below the eutectic transition temperature at a rate of $21\,^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$; then, once stabilized, the furnace temperature was increased to (20 or 10) °C above the fixed-point temperature, ramping at a rate of $24\,^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$. After completion of the melting plateau, the furnace was cooled below the fixed-point temperature to complete freezing.

4.3 Uncertainties

The following uncertainty contributions were considered. Based on the standard deviation of measurements during 1 day, the repeatability of a cell was taken to be 20 mK.

Based on the variation in realization on different days, the radiation thermometer short-term stability during the comparison was taken to be 40 mK. By inspection of the melt curves, the uncertainty of the melting inflection point temperature determination was estimated to be 25 mK. From the difference in the calculated emissivity of the cells, the uncertainty component due to non-blackbody conditions is taken as 10 mK [16].

4.4 Results

Figure 7 shows typical melting plateaux for the NIM and NPL cells with the ±20 °C furnace temperature step. The average melting temperatures for each day and comparison results are shown in Table 3 and Fig. 8. Agreement between the NIM and the NPL Pt–C cells was better than 40 mK with a combined uncertainty of 105 mK ($k = 2$).

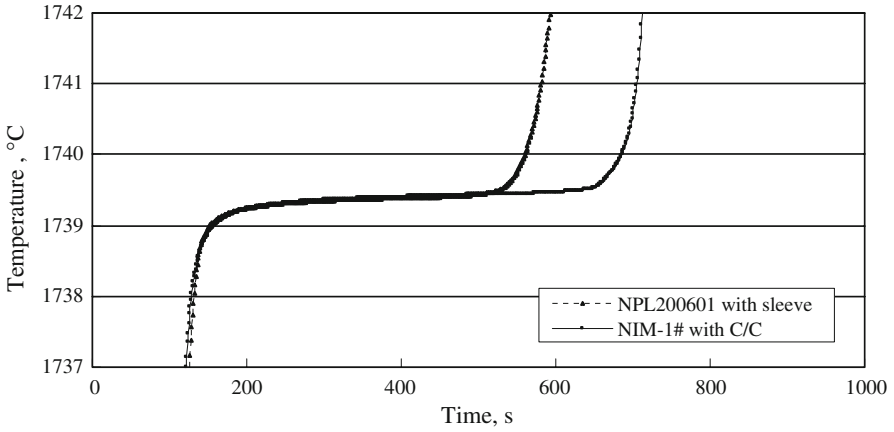

Fig. 7 Melt curves for NIM 1# Pt–C and NPL 200601 Pt–C

Table 3 Comparison of the Pt–C fixed point between NIM and NPL

	Melting inflection temperature (°C)/SD (°C)					T_{average} (°C)
(Date/2006)	22 June	26 June	27 June	28 June	29 June	
NIM1#	1739.424/ 0.007		1739.439/ 0.009		1739.432/ 0.011	1739.432
NPL200601		1739.389/ 0.010		1739.398/ 0.010		1739.394
$T_{\text{NIM1\#}} - T_{\text{NPL200601}}$						38 mK

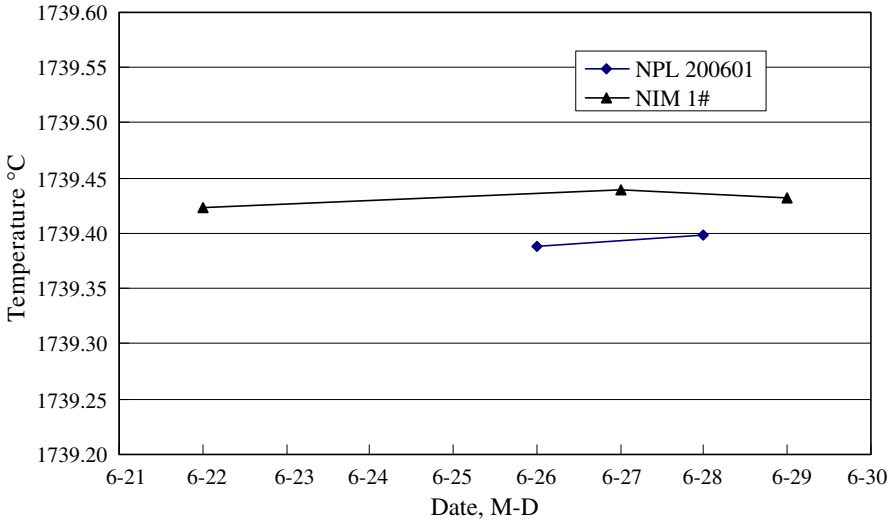

Fig. 8 Average melting temperature as a function of the date of measurement

5 Discussion

Two Pd–C cells were broken during filling. It seems the metal could not inosculate well with the carbon of the crucible, whether this was because of poor temperature uniformity of the furnace needs further investigation.

We know from temperature uniformity measurements that we can move the crucible in the furnace while the melt or freeze is being performed, so perhaps a crucible extension can be used for filling by moving the cell through the hottest zone and having the metal melt always from the top down and freeze from the bottom up to solve both the problems of temperature uniformity and to speed up crucible filling. Further, we can imagine that it is possible to mechanically shake the graphite stick supporting the crucible without disturbing the furnace, so that molten metal settles successfully in the crucible bottom from the crucible extension.

We can see from Fig. 7 that the plateau of the NIM cell is longer than that of the NPL cell, although it contains less metal—46 g compared to 69 g. This is thought to be due to the thermal insulation of the C/C sheet.

6 Conclusion

(a) A modified Thermogauge furnace that can be used vertically can produce good cells, if care is taken that the melting of the metal always starts from the top and freezing from the bottom, and preferably with a relatively rapid rate of melting.
(b) The comparison result of Pt–C shown here and other published values indicate that the goal of reproducibility of 100 mK above 2,300 K is certainly achievable.
(c) Further confirmation is given that C–C sheet can produce the same plateau duration and shapes with a reduced amount of metal.

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