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Experience of Construction and Study of Pt–C Eutectic in VNIIM and Cooperation with LNE-INM

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Abstract A new high-temperature furnace was developed in VNIIM and manufactured by the Omsk plant "Etalon." This furnace is intended for the realization of various fixed points of pure metals and high-temperature metal–carbon eutectics up to a temperature of 3000°C. The construction of the furnace allows measurements to be carried out either with or without the protective window, in a protective atmosphere of argon. The furnace will be described in this article. Cooperation with LNE-INM was initiated with the aim of sharing experience in metal–carbon eutectic cell construction and comparing two Pt–C cells (one cell was made by each partner) as a means of comparing scale realizations around 1740°C. The filling technique used in each laboratory will be described. The average melting temperature of the VNIIM Pt–C eutectic cell, characterized and studied at VNIIM, was 1738.4°C with a standard uncertainty of about 0.13 K. The repeatability of the melting temperature with various measurements was estimated to be within the limits of (0.02–0.2) K. The cell supplied by LNE-INM is the one that was constructed and studied in the framework of the HIMERT European project and described elsewhere. The difference in the melting temperatures of the fixed points (VNIIM—LNE-INM) is about 0.4 K with a standard uncertainty not exceeding 0.18 K. The cells constructed and characterized by each partner were exchanged and measured by the other partner. The results of the study of the melting and freezing of the Pt–C cells carried out by VNIIM and LNE-INM will be presented. The reasons for the difference in the melting temperatures of the two

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cells are analyzed, and the steps preceding the comparison of the scale realizations of the two laboratories are presented.

Keywords Blackbody · Fixed point · Furnace · High temperatures · Melting · Metal–carbon eutectics · Temperature scale

1 Introduction

Requirements of high accuracy at the highest temperatures dictated by the development of science and industry stress the need for high-temperature references. Metal–carbon eutectic points have been developed and studied in recent years [1–3] and may be convenient as fixed points of a new temperature scale. The present work was undertaken to determine the accuracy obtainable with a Pt–C eutectic under various conditions and with different equipment.

Cooperation with LNE-INM was initiated with the aim of sharing experience in metal–carbon eutectic cell construction and comparing two Pt–C cells (one sample was constructed by each partner) as a means of comparing scale realizations around 2000 K.

2 Equipment

The high-temperature furnace HTBB-30/900/2500 was developed to enable research in the temperature range above the freezing point of copper. It is a furnace with a tubular graphite heater through which an electrical current passes to directly heat the element. Water cooling and both manual and automatic control of the system are provided.

Two views of the installation are presented in Fig. 1. The furnace consists of a resistance appropriate to the model of blackbody, cooling system, power supply (transformer, control unit), a feedback pyrometer, and an argon supply system. The construction provides for possible emergencies arising from malfunctions of the mains voltage and water supply, and contains control relays ensuring safety interlocks are applied in case of inadmissible conditions.

Structurally, the heaters represent two symmetrical tubular pieces. There are three possible heater variants (see Fig. 2):

1. Simple heater intended for calibration in the temperature range from 900 to 2300°C (short-term—up to 2500°C).
2. Heater with an extended heating zone intended for precision calibrations in the temperature range from 900 to 3000 °C.
3. Heater with a container for crucibles intended for the fixed points of pure metals and eutectic alloys, in the temperature range from 900 to 3000°C.

The conical insert located inside the “simple heater” and the “heater with extended heating zone” plays the role of the bottom of a radiating cavity and simultaneously

Fig. 1 Photographs of the furnace

connects the tubes with a screw coupling. In the case of the "heater with a container for a crucible," the container itself forms the fastening element.

The sizes of the cavities and the power consumptions are listed in Table 1. The three configurations of heaters are schematically represented in Fig. 2.

The furnace housing is a cooled cylindrical tank with massive current leads. Thermal insulation to diminish the heat loss is located inside the tank and around the heater. The thermal insulation (graphite felt) is located between two graphite heavy-walled cylinders. Pipe connections for water cooling are located on the front flange. The back current lead is located in a protective shell, isolated from the furnace housing. To improve electrical contact with the heater, a spring is used in the construction of the current lead. There is a pipe connection for argon to create an inert atmosphere around the graphite heater in order to avoid oxidation (above ∼400°C).

The power to the heater is governed through a thyristor by the external controller. The control is carried out with an impulse shifted in phase with respect to a half cycle of the mains voltage. The phase angle determines the power given to the heater.

A feedback pyrometer fixed on a bracket looks at the back part of the conical insert (or crucible container) through the protective window as input to the PID controller, allowing the furnace to be stabilized at the desired blackbody temperature.

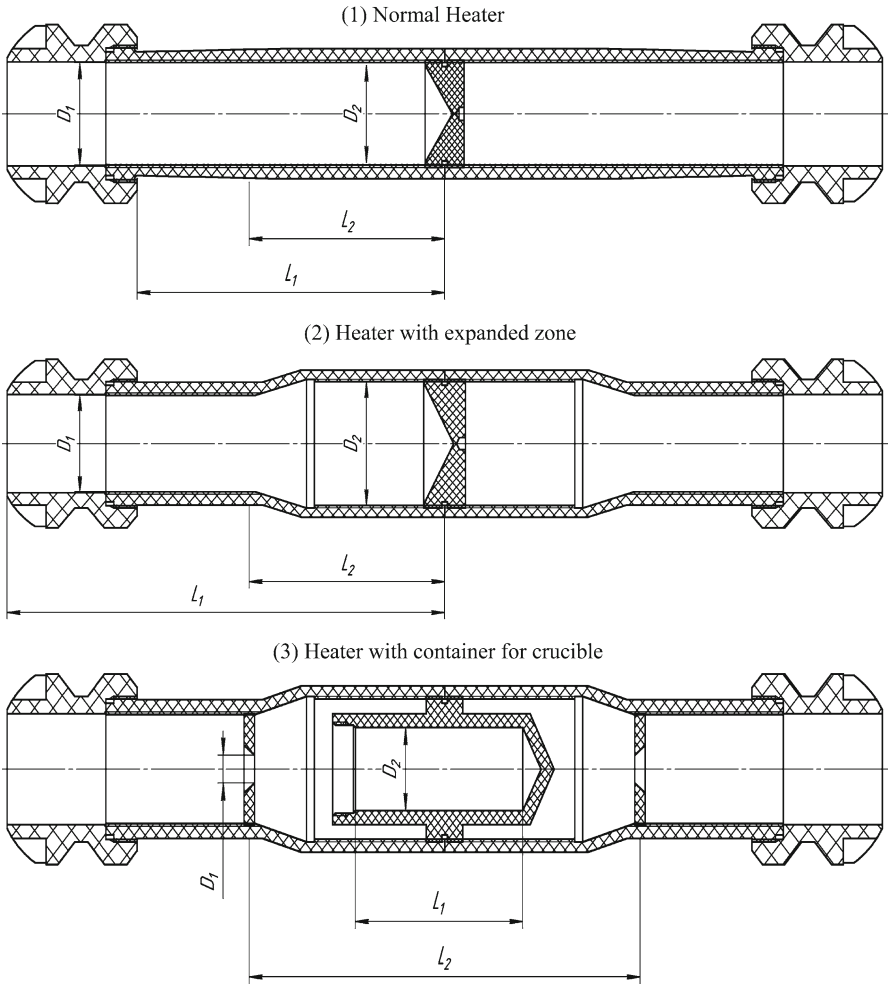

Fig. 2 Drawings of the heaters

Table 1 Dimensions of heaters and the furnace power consumption

Variant of heater	D1 (mm)	D2 (mm)	L1 (mm)	L2 (mm)	Temperature regime (°C)	Power (kW, maximum)
Simple	30	30	150	75	900/1500/2000/2500	3/6/12/18
With expanded heat zone	30	40	150	75	900/1500/3000	4/9/21
With container for crucible	10 (20)	24[a] (4[b])	64[a] (40[b])	150[a]	900/1500/3000	4/9/21

[a] In accord with cell size
[b] To ensure characteristics, if it is required

3 Description of Work at VNIIM

3.1 Cell Construction

The procedure to fill a crucible is similar to the description in [4,5]. The specially purified platinum powder (99.999%) was mixed with graphite powder of high purity (99.9999%) to obtain a proportion (by mass) of 1.2% carbon [6]. The platinum powder had a "spongy" structure; that is, the grains were porous and consisted of grains of various lengths. The graphite powder had a homogeneous structure consisting of smaller grains.

The platinum–graphite mixture was poured into a crucible whose design is shown in Fig. 3a. The crucible was located in a vertically oriented furnace and was heated to 1685–1690°C. This condition was maintained for 30 min. Then, the furnace was cooled to room temperature; this procedure was necessary for the initial sintering of the eutectic components. At this stage of the eutectic creation, the baked powder had a porous, massive, rigid structure (based on visual observations when opening the crucible).

Then, the crucible was heated to 1765–1770°C; that is, approximately 30 K higher than the eutectic melting point, or practically to the melting temperature of pure

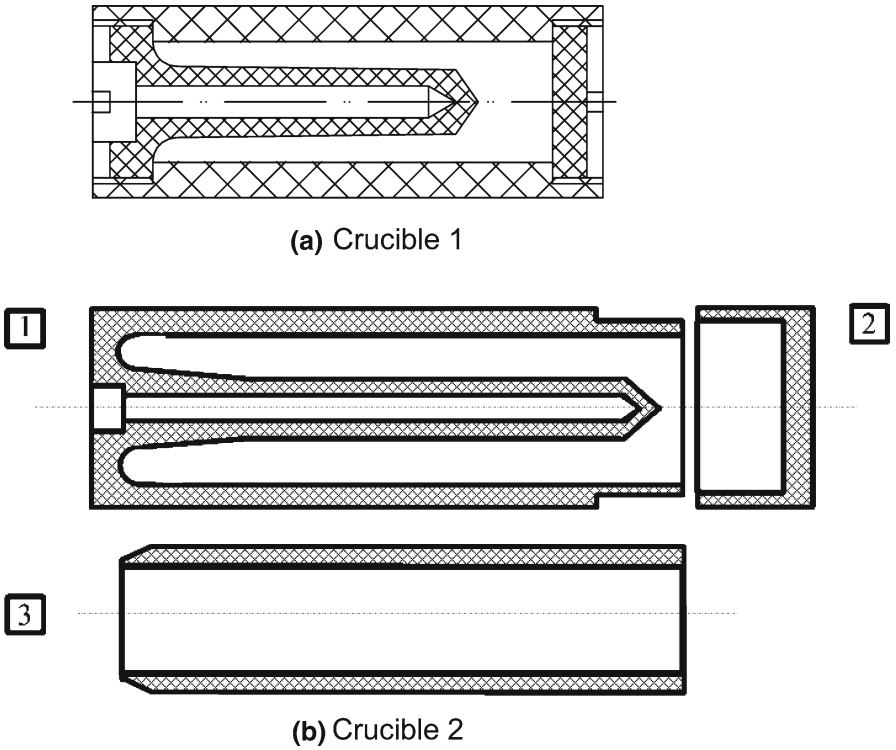

Fig. 3 Drawings of the crucibles

platinum. This condition was maintained for 10 min, and then the furnace was smoothly cooled to room temperature. Then, the filling procedure was repeated. The filling of the crucible at the last stage was carried out with application of a special graphite hub (thin-walled graphite tube, permitting the filling of the mixture without removing the crucible from the furnace). After the filling of the crucible was completed, the furnace was returned to the horizontal position, and the temperature control parameters to realize the Pt–C eutectic melting point were set.

Melting and freezing plateaux of the Pt–C eutectic were obtained, but soon the external envelope of the crucible was destroyed because of the sticking of platinum to the graphite walls of the crucible. The outer envelope broke due to the mechanical stresses from repeated thermal expansion/compression with the heating/cooling cycles.

A new crucible was constructed on the basis of LNE-INM's cell, see Fig. 3b. The crucible consists of three elements. The envelope of the crucible is hardly connected to the pin (1), the small gap between the envelope of the crucible and the cover (2) ensures good fixing and accommodates the volume increase at the phase change. To damp the forces originating from thermal expansion of the ingot and make contact with the graphite walls of the envelope, an inner sleeve (3) is added.

The graphite material for all elements is "Isostat DE-24." The platinum–carbon alloy from the broken crucible was remelted into the new crucible with the application of a specially developed adapter. The melting was carried out at a higher furnace temperature (20–30 K above the melting point of platinum). This was necessary because the length of two crucibles plus the adapter was greater than the extended zone of the heater.

After remelting, the crucible was located in the horizontally positioned furnace and the initial melting was carried out. Unfortunately, the eutectic melting and freezing plateaux were not observed, as in the old crucible. Apparently, the structure of the ingot in the cell was modified during remelting. To restore it, a series of procedures was undertaken. The crucible was located in the furnace and was heated to 20–25 K above the eutectic point. This condition ("annealing") was maintained for 4–5 h. Then, the furnace was switched off and the crucible was rapidly cooled to a temperature approximately 10–15 K lower than the eutectic point temperature. After that, the furnace was set to smoothly reduce the temperature to room temperature. The same procedure was repeated a number of times. After the total "annealing" time reached 30 h, the melting and freezing plateaux were observed. The durations of these plateaux were brief, about 20–30 s, and the slope of the curves was large. Apparently, this may be explained by there being a small proportion of eutectic alloy relative to the total amount of material. When the duration of the annealing reached 60–70 h, the Pt–C eutectic was restored.

The melt improvement obtained in our experiment (smaller slope and longer duration) with repeated melts under the same conditions can be explained by an increase in the fraction of eutectic, and is similar to the results shown in [7] where the dynamics of repeated "melting-freezing" cycles under the same conditions are considered. The essence of the supposed mechanism is the memory of the ingot structure from the previous freezing; each subsequent melting-freezing cycle increases the fraction of eutectic zones in an alloy (the first conjecture and exposition of such a mechanism known to us is in [8]). As we are sensing the average temperature of the crucible volume, the

melting behavior improves. The destruction of the cluster structure happens faster the more the melted ingot is overheated. Such behavior is even more apparent for pure metals [9].

With the "refilling" to another crucible, a large overheating took place, and structural eutectic zones favorable to the creation of a eutectic alloy were destroyed. Simultaneously with the restoration of the eutectic, optimization of the parameters of the furnace controller and of the temperature field in the vicinity of the crucible was carried out. In particular, with the purpose of improving conditions for eutectic alloy formation in the majority of the ingot volume and the phase-transition quality, experiments were carried out to determine the number and positions of auxiliary diaphragms to ensure the temperature uniformity in the crucible zone. As an outcome, the parameters to realize the best plateaux were defined.

3.2 Procedures

The temperature of the Pt–C eutectic fixed point was determined by comparison with a standard gas-filled tungsten strip lamp. The melting and freezing plateaux were measured with an effective wavelength $\lambda_{\text{eff}} = 656.3\,\text{nm}$ and bandwidth $\Delta\lambda = 4.5\,\text{nm}$ using a single-channel spectral comparator with mirror optics, a double monochromator, and a thermally stabilized Hamamatsu S6204-01 silicon photodiode.

The calibration of the measuring system was carried out with a copper fixed point, reproducing a temperature defined by the ITS-90. The linearity of the radiance measurement was checked by the method of flux doubling. The size-of-source effect (SSE) was estimated by means of a variable diaphragm. The uncertainties caused by nonlinearity of the signal and the SSE were evaluated as 20 and 80 mK, respectively (in terms of the half-width of a supposed rectangular distribution).

During the comparison, the temperature of the furnace containing the Pt–C cell was stabilized for approximately 15 min at 6–10 K below the eutectic melting temperature. Then, the temperature of the furnace was increased by 10–15 K, and the melting plateau was recorded by the photodiode signal. After the melt, the furnace temperature was stabilized approximately 15 K higher than the eutectic melting point. In parallel, the current in the standard lamp was determined by measuring the lamp radiance (the photodiode signal). From the calibration characteristic of the lamp, the temperature was derived.

After maintaining the ingot stabilization temperature for 15–20 min, the cooling of a furnace was carried out and the Pt–C eutectic freezing plateau was measured. After that, the temperature of the furnace was stabilized approximately 7–10°C lower than the melting temperature and another cycle of measurements was carried out.

3.3 Results

A series of melting plateaux of the Pt–C eutectic was recorded for the VNIIM cell, some of which are shown in Fig. 4a (the time scale was corrected to facilitate the comparison of different plateaux). The temperature equivalent of the photodiode output sensitivity at 1750°C is $0.3\,\text{K}\cdot\text{mV}^{-1}$. When the additional diaphragms (in front of

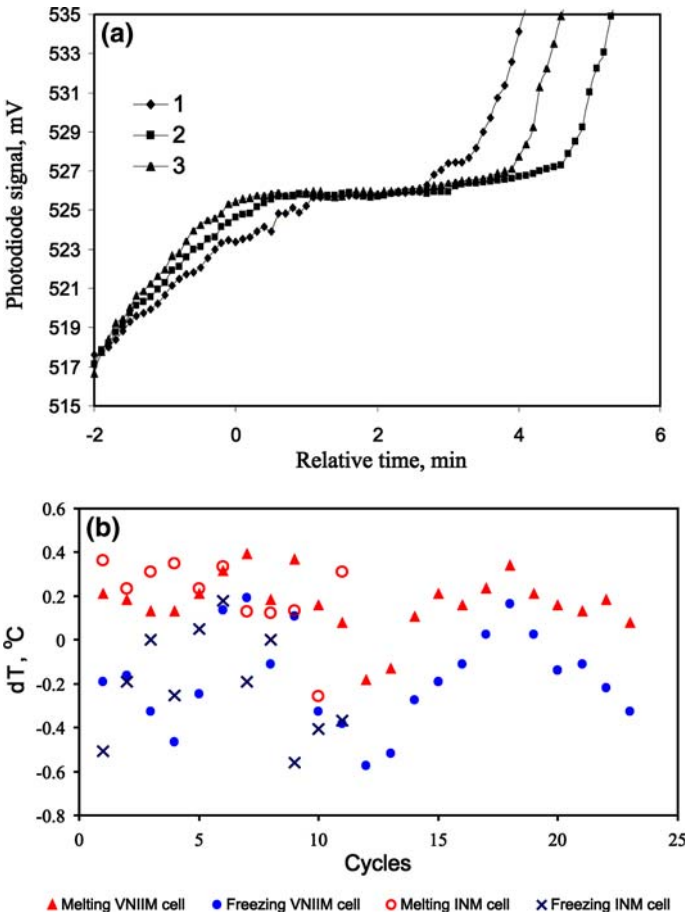

Fig. 4 Results of the experiments with Pt–C: (**a**) diaphragms' influence on Pt–C melting curves: curve 1—the additional diaphragms are absent; curve 2—an appropriate positioning of the diaphragms and an appropriate heating rate for the cavity; and curve 3—the additional diaphragms are present and properly located, but the overheating is too large and (**b**) deviations from average values of melting and freezing temperatures of Pt–C eutectic

the crucible) in the cavity of the heater with the extended zone are absent, the plateau corresponding to curve 1 was obtained; in curve 3, the additional diaphragms are present and properly located, but the overheating is too large. Curve 2 corresponds to an appropriate positioning of the diaphragms and an appropriate heating rate for the cavity.

3.3.1 Temperatures

Twenty-two cycles of measurements with the VNIIM cell and 11 with the LNE-INM cell were carried out. The deviation from the average value of the melting and freezing temperatures for both cells are shown in Fig. 4b, where the freezing temperature was

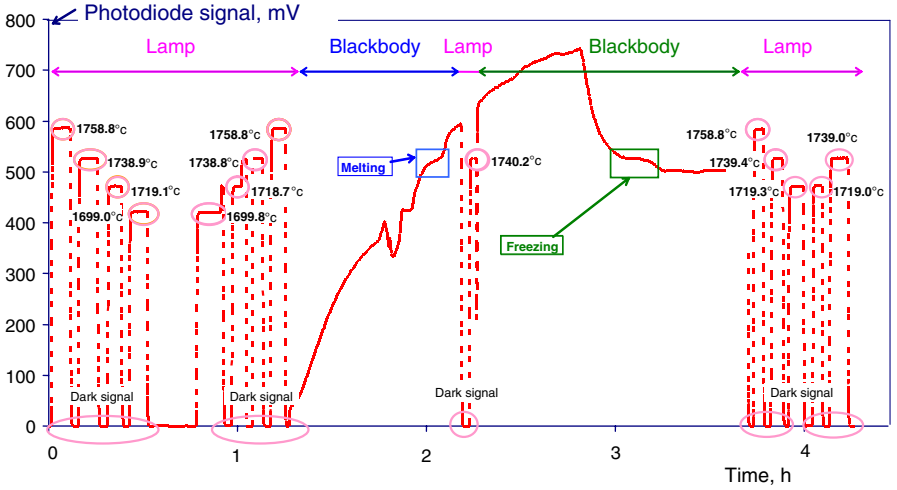

Fig. 5 Comparison of a Pt–C eutectic cell with a standard lamp

defined as the maximum of the freezing curve and the melting temperature was defined as the point of inflection (minimum of dT/dt) of the melting curve.

A curve comparing the LNE-INM Pt–C cell with the VNIIM standard lamp is presented in Fig. 5. The average melting temperatures appear to be 127 and 160 mK above the freezing temperatures for the VNIIM cell and the LNE-INM cell, respectively, and the maximum deviation from the average was 220 mK. The average melting temperature of the VNIIM cell was 1738.4°C with a standard deviation of 130 mK, and the average freezing temperature was 1738.2°C with a standard deviation of 220 mK. For the INM cell, these values are 1738.0°C with a standard deviation of 180 mK and 1737.8°C with a standard deviation of 240 mK, respectively.

The difference between the cells is more than the estimated uncertainty. It is possible that this difference is attributable to a difference in the thermal conductivity of the graphite of the cells combined with heterogeneity of the temperature field in the furnace.

3.3.2 Uncertainties

Estimation of the combined uncertainty u_c, represented as the standard deviation of the sum of the Type A and B uncertainties associated with various influence factors estimated both from our experimental data and from other studies [7–9], is calculated by the formula,

$$u_c = 2\sqrt{u^2 + \sum_{i=1}^{14} u_i^2},$$

The uncertainty components (in terms of the standard deviation) are enumerated in Table 2. In view of the estimated values of the components, the expanded combined

Table 2 Uncertainty budget

Source of uncertainty	i	u_i (mK)
Uncertainty of standard lamp (calibrated at copper point)	1	75
Impurities in Pt–C eutectic	2	17
Correction of temperature drop across the crucible wall	3	26
Plateau identification	4	58
Photodiode output signal drift	5	6
Emissivity of blackbody	6	20
Size-of-source effect	7	46
Nonlinearity of photodiode	8	12
Environmental conditions (influence on standard lamp)	9	52
Signal ratio	10	46
Lamp current measurement	11	35
Interpolation of temperature via lamp current	12	46
Nonrepeatability of elements of the optical scheme and the lamp comparison	13	46
Zero instability at eutectic point	14	6
Expanded combined uncertainty ($k = 2$) at standard deviation u=130 mK		*410*
Expanded combined uncertainty ($k = 2$) at standard deviation u=240 mK		*580*

uncertainty u_c (at $k = 2$) ranges from 410 to 580 mK, depending on the standard deviation of the plateau (i.e., melting or freezing, and either the VNIIM or the LNE-INM cell).

The obtained result supports further use of the eutectic cell to increase the realization and dissemination accuracy of the temperature scale.

4 Description of Work at LNE-INM/CNAM

4.1 Pt–C Cell Construction, Characterization, and Results

The Pt–C cell studied during this collaboration is the first Pt–C constructed at LNE-INM in the framework of the European project HIMERT [10]. The platinum used was purchased from Alfa-Aesar in the form of powder with a nominal purity of 99.999%. The graphite powder used to form the eutectic alloy was purchased from the same company and the claimed nominal purity is 99.9999%. The crucible was machined from graphite with a 30 ppm concentration of impurities (ash). The design of the crucible is the same as in Fig. 3b. The filling was done with LNE-INM's HTBB 3200 PG positioned vertically. Seven filling steps were necessary to complete the filling. The composition of the metal–carbon mixture for each of the filling steps varied from 0 to 0.8% by mass of C in Pt, all below the eutectic composition (1.2 mass% C in Pt).

The Pt–C mass at the end of the filling process was not less than 75.8 g in a volume of about 3.9 cm^3. After the completion of the filling process, the Pt–C cell was characterized. A series of melting plateaux were measured (see Fig. 6) and the repeatability of the inflection point of these plateaux (excluding the first plateau) was as low as 15 mK.

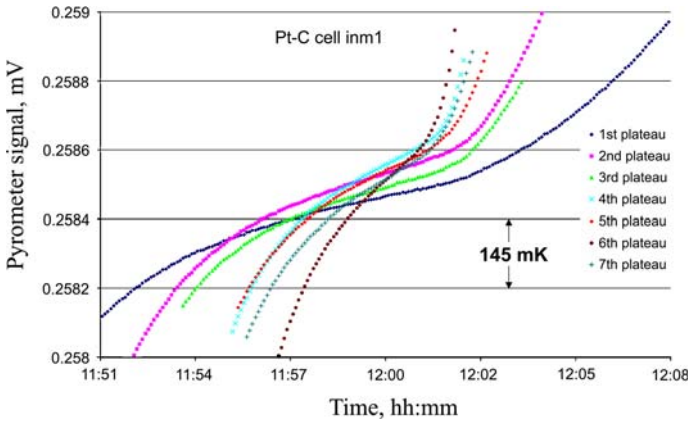

Fig. 6 Plateaux obtained with LNE-INM's Pt–C cell to estimate the repeatability of the melt

The melting-temperature measurement was done in terms of ITS-90 with a calibrated KE LP3 radiation thermometer [11]. The temperature obtained, (1737.5 ± 0.6)°C was evidently affected by the furnace nonuniformity. Subsequent measurements performed with this cell during a comparison at PTB in a better thermal environment (Nagano/Chino-type furnace of improved temperature uniformity) resulted in higher temperatures (and was measured in terms of thermodynamic temperature) [12]. The temperature obtained was (1738.51 ± 0.3)°C.

4.2 Measurement of VNIIM's Pt–C Cell

A series of melt and freeze cycles were obtained for VNIIM's Pt–C cell while LNE-INM's cell was being studied by VNIIM. The furnace was not optimized at that time for temperature uniformity. The melting range we observed in these conditions was significant (about 1°C), but very good repeatability of the inflection point of the melts was obtained (18 mK). The ITS-90 mean melting temperature of this cell was determined to be (1738.0 ± 0.6)°C.

5 Conclusion

One Pt–C cell constructed by LNE-INM and one by VNIIM were measured by each of the laboratories. The initial idea was to exchange experiences with the construction and the study of this high-temperature fixed point. It also provided an opportunity to check if the differences in terms of ITS-90 realization are significant. The differences in temperature lie within the uncertainties and are not significant; however, the uncertainties are affected by the thermal environment of the cell and it would be much more compelling to perform the measurements in the same furnace within a short time period. Differences in the thermal environment may explain the huge difference in the repeatability of the melting temperature obtained by the two laboratories (0.2°C at VNIIM and 0.02°C at LNE-INM).

This collaboration between the two laboratories in the field of high temperatures will continue to further assess important effects influencing the measurement of high temperatures (ITS-90 and thermodynamic temperature) as well as the implementation of metal–carbon eutectic points.

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