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High-Temperature Fixed-Point Facilities for Improved Thermocouple Calibration—Euromet Project 857

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Abstract LNE, NPL, and PTB decided in 2005 to join their research efforts in the framework of Euromet Project 857 with the aim of reducing the calibration uncertainty of noble metal and other high-temperature thermocouples by at least a factor of two. This ambitious target will be met through the development and implementation of robust high-temperature fixed points based on metal–carbon eutectic technology. The Euromet project is structured around five work packages and ensures good and efficient cooperation between the partners to meet the objectives within the project timeframe of four years. Furthermore, a formal cooperative research agreement has been established with the National Metrology Institute of Japan (NMIJ) to demonstrate, on a worldwide basis, that this new method is a significant improvement over current calibration methods. In summary, the project consists of (a) the development of sets of cells at the cobalt–carbon eutectic point (1,324°C) and palladium–carbon eutectic point (1,492°C) and (b) the construction of platinum/palladium (Pt/Pd) thermocouples carefully stabilized for use to these temperatures. Supplementary research to be undertaken as part of this project is the improvement of fixed-point construction and realization capabilities through high-temperature furnaces with low thermal gradients. This paper describes the European project and gives an overview of current progress.

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1 Introduction

The best measurement uncertainty for the calibration of noble metal thermocouples (currently Types R, S, or B) at high temperatures is ±0.3°C at 1,000°C rising to ±1.5°C at 1,500°C. Calibration below 1,100°C can be performed using metal fixed points (Ag, Au, or Cu) having assigned temperatures on the ITS-90. The larger uncertainty at higher temperatures is primarily due to the lack of reliable, high-temperature fixed points. Calibration is generally performed at 1,554°C using the so-called 'wire bridge method' at the Pd melting point, a secondary fixed point. This calibration technique is destructive and consists of breaking the thermocouple hot junction and welding a palladium (Pd) wire between the thermoelements. This assembly is subsequently heated in a furnace and the emf monitored. If the heating rate is slow enough, a plateau is observed when the Pd wire melts—this provides the reference for the calibration. It is highly desirable to replace the Pd-wire point, partly because of the large uncertainty it introduces into the calibration, but also because it is a destructive method that necessitates disassembly of the thermocouple under test.

Ideally, the calibration at high temperatures would be performed in a fixed-point cell, just as at lower temperatures. Novel high-temperature fixed points based on metal–carbon eutectic alloys [1–3] have been shown to be high-performance temperature standards above the freezing point of Ag (962°C), and their use could certainly reduce the scale-realization uncertainties [4] and address practical thermometry needs [5–10]. A good overview of the current state of research with respect to high-temperature fixed points (HTFP) can be found in [11].

Recent comparisons of metal–carbon fixed points constructed for contact thermometry applications have shown unprecedented agreement in this temperature range (within 0.1 K), indicating that these HTFPs can serve as practical and repeatable standards [12,13]. Research in this area within the European Union (EU) has been performed on a cooperative basis [4]. As a continuation of the joint research initiated in 2001 [14,15], LNE, PTB, and NPL have agreed to cooperatively develop robust HFTP facilities for the routine calibration of thermocouples with uncertainties reduced by at least a factor of two compared to current capabilities. This research is carried out within the framework of Euromet Project 857, "High temperature fixed points for improved thermocouple calibrations," which started in July 2005. The objectives of the project are to:

- increase confidence in the accredited thermocouple calibration service through fully assessed fixed-point cells, rather than relying on a piece of Pd wire of uncertain purity;
- provide a means to compare national temperature measurement capabilities with lowest uncertainties;
- enable selection of the most appropriate calibration method and temperature range required by the user.

A cooperation agreement between the project partners and the National Metrology Institute of Japan (NMIJ) has been agreed with the aim of qualifying, on a worldwide basis, these new devices for their implementation as improved alternatives to current thermocouple calibration methods.

2 Description of Project

Each project partner will construct a set of contact thermometry cells at the cobalt–carbon (Co–C) eutectic fixed point (1,324°C) and, subsequently, at the palladium–carbon (Pd–C) eutectic fixed point (1,492°C). These plans require new fixed-point realization capabilities through the use of high-temperature furnaces with low thermal gradients and the development of robust Pt/Pd thermocouples. The latter will be used initially for cell characterization and comparison but, ultimately, the partners aim to use these devices as instruments for interpolation between fixed points and for dissemination of high-temperature scales to industrial calibration laboratories.

The EU partners aim, within four years, to integrate all these developments into their routine calibration activities. This is only possible through the pooling of resources and facilitating continuous collaboration between the partners. Part of this work is associated with a demonstration ‘Quickstart’ EU project showing the value of collaborative research.

2.1 Structure of the Project

The project is divided into five work-packages. Work-package 1, led by PTB, concerns the development of Pt/Pd thermocouples. Work-package 2, led by LNE, is dedicated to the development of a set of seven Co–C eutectic cells (1,324°C). Work-package 3, led by NPL, concerns the development of a set of Pd–C eutectic cells (final number to be decided). The traceability to ITS-90 will be assessed in Work-package 4, led by NPL. Work-package 5, led by LNE, deals with project management, the organization of meetings, and a workshop (HTFP 2006, Paris, June 2006), as well as developing future industrial dissemination plans.

2.2 Description of Work

Technical activities started at the beginning of 2006 with the construction of Co–C eutectic cells and Pt/Pd thermocouples. At least three thermocouples per laboratory were constructed and assessed for thermoelectric stability and homogeneity. Two Co–C eutectic cells are to be constructed by each of the partners, in addition to a seventh cell constructed by LNE for long-term stability assessment. The Pt/Pd thermocouples are intended for local tests of the Co–C eutectic cells.

Following construction and local test of the Co–C fixed-points, a comparison of cells will be performed, including cells from NMIJ, to assess their stability and reproducibility. For this comparison, each participating laboratory, including NMIJ, provides one Co–C eutectic cell. The four cells and two thermocouples selected on the basis of their performance will circulate to the laboratories in the following order: PTB, NPL, LNE, NMIJ, and PTB.

It is also currently planned to measure by radiation thermometry the second Co–C eutectic cell constructed in each laboratory to establish traceability to ITS-90. Additional measurements with Pt/Pd thermocouples will be made to take into account the influence of the variable conditions of use by each partner. Assessment of this fixed point is planned to end by mid-2008.

The development of Pd–C eutectic cells will start by mid-2007. It will follow the same steps as for the Co–C eutectic point and be based on the experience gained in the previous work. Investigation of this fixed point is planned to end by mid-2009.

3 Technical Progress

Early results on high-temperature fixed points, associated high-temperature furnaces, and Pt/Pd thermocouples are presented below.

3.1 Co–C Cells

At this stage of the project, two Co–C cells have been constructed in each laboratory.

3.1.1 Crucible Design

The characteristics of the cells constructed within this project are given in Fig. 1 and Table 1. Cells were constructed using crucibles based on a modified PTB design [12] to meet the requirements of the present project (Fig. 1a, b). A supplementary cell was constructed by LNE with a specific crucible design (Fig. 1c). The dimensions of these

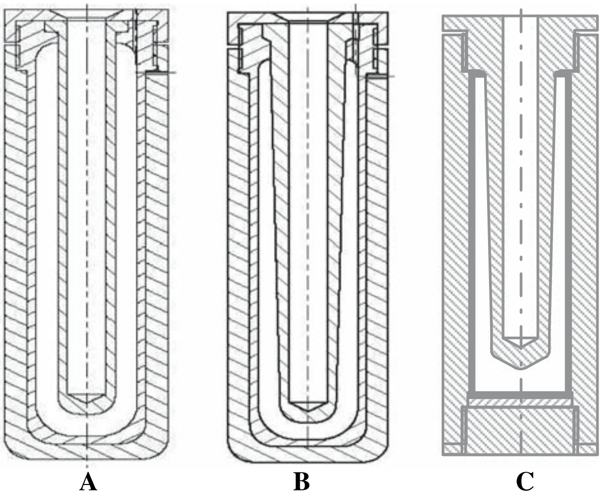

Fig. 1 Cobalt–carbon eutectic cells: (**A**), (**B**), (**C**)—different designs

Table 1 Dimensions of the Co–C cells

Crucible	Inner diameter (mm)	Inner length (mm)	Outer diameter (mm)	Outer length (mm)
(a)	9	106	37	125
(b)	9	108	37	125
(c)	9	91	40	125

Table 2 Impurity analysis of cobalt powder in ppm (mass fraction) (major metallic impurities in bold)

Element	Li	B	C	N	O	Na	Mg	Al	Si	P	S	Cl	Ca	Ti	V
(ppm)	0.05	0.2	120	0.6	900	0.02	**4**	**5**	0.1	0.04	0.5	**7**	**20**	0.7	0.02
Element	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As	Sr	Y	Zr	Te	Pt	Pb	Bi
(ppm)	0.09	0.3	**5**	0.8	0.4	0.4	0.5	1	0.9	**5**	0.3	0.07	1	0.7	0.07

cells allow their use in the vertical position with thermocouples of up to 7 mm outer diameter. The minimum wall thickness of the thermometer wells is 2 mm. The cells of designs (b) and (c) have a conical shape for the re-entrant well to facilitate operation in the horizontal position. The design includes a sacrificial lining sleeve to reduce the possibility of outer crucible breakage.

3.1.2 Cell Materials

The high-purity graphite crucibles (grade R6710) were supplied by SGL Carbon and had an ash content of less than 5 ppm. Cobalt powders of 99.998% and 99.999% nominal purities were supplied by Alfa Aesar and Sigma Aldrich, respectively. Graphite powder, also supplied by Alfa Aesar, had a nominal purity of 99.9999%. An impurity analysis of the metal provided by Alfa Aesar was performed by the NRC using glow discharge mass spectrometry (GDMS). The result of the analysis, presented in Table 2, indicates a purity of about 50 ppm (mass ratio metals basis). The measured purity is somewhat lower than that claimed by the manufacturer. However, the measurement uncertainty as indicated in the NRC certificate is at “a factor of 2.”

3.1.3 Filling Procedure

Before filling, the crucibles were baked 4 h at 1,400°C in vacuum (4×10^{-4} Pa) at PTB, 8 h at 1,450°C in argon at NPL, and 3 h at 1,800°C in vacuum ($1–5 \times 10^{-2}$ Pa) at LNE. The metal–carbon powder mixture was prepared at approximately 2.5% mass fraction of carbon. Crucibles were filled in an argon atmosphere at PTB and NPL, and in vacuum ($1–5 \times 10^{-2}$ Pa) at LNE. Crucibles were heated approximately 15 K above the melting temperature of the Co–C eutectic powder mixture. This temperature was maintained for about 1 h to enable good diffusion of the carbon in the liquid state. The temperature of the furnace was then reduced by 30 K in a stepwise manner to solidify the ingot before cooling (about $10\,\mathrm{K \cdot min^{-1}}$ or less) to room temperature. Filling of

Table 3 Cobalt–carbon cells and characteristics

Institute	Designation	Corresponding diagram (Fig. 1)	Cobalt provider	Mass of alloy
LNE	CoC-L-2	B	Alfa Aesar	167 g
	CoC-L-3	B	Sigma Aldrich	183 g
	CoC-L-4	C	Alfa Aesar	n.y.a.
PTB	Co-C3/PTB	B	Alfa Aesar	164 g
	Co-C4/PTB	A	Alfa Aesar	205 g
NPL	NPL/Co-C1	B	Alfa Aesar	163 g
	NPL/Co-C2	B	Alfa Aesar	163 g

each crucible (Fig. 1a and b) was completed in six cycles. A supplementary cycle was necessary to insert the thermometer well in the molten alloy. After construction, small cracks were noticed on the inner ‘sacrificial’ sleeve (see crucible description above). Details of the cells constructed and the masses of the Co–C alloy are given in Table 3. The density of the Co–C alloy was measured using two small ingots constructed separately from the HTFP cells to assess the amount of mixture required for optimal filling of the crucible. The density was found to be $8.0\,\mathrm{g\cdot cm^{-3}}$ at 23°C (hypo-eutectic).

3.2 High-temperature Facilities

Past experience has demonstrated that the thermal environment has a strong influence on the performance of metal–carbon cells. Therefore, particular attention was paid to furnace-temperature uniformity.

3.2.1 LNE Furnace Arrangement

The new high-temperature furnace of LNE (Fig. 2) was developed in cooperation with NMIJ and the manufacturer (Mattels). It consists of a vertical atmospheric furnace for use with metal–carbon cells up to 1,500°C. The heater elements are composed of 32 silicon-carbide rods distributed in three zones to ensure good temperature uniformity along a high purity alumina tube (outer diameter of 80 mm, inner diameter of 70 mm, length of 1000 mm) containing the crucible and associated insulation. The alumina tube is equipped with airtight flanges on both sides. The upper flange allows for the insertion of Pt/Pd thermocouples under a continuous purge of high-purity argon (1 ppm max. impurities) slightly above atmospheric pressure. The cell, placed centrally in the furnace, is surrounded by graphite insulation and graphite mounting blocks. The temperature distribution over the length of the crucible was measured and found to be uniform to better than ±0.2°C at 1,324°C (Co–C eutectic point) and at 1,492°C (Pd–C eutectic point).

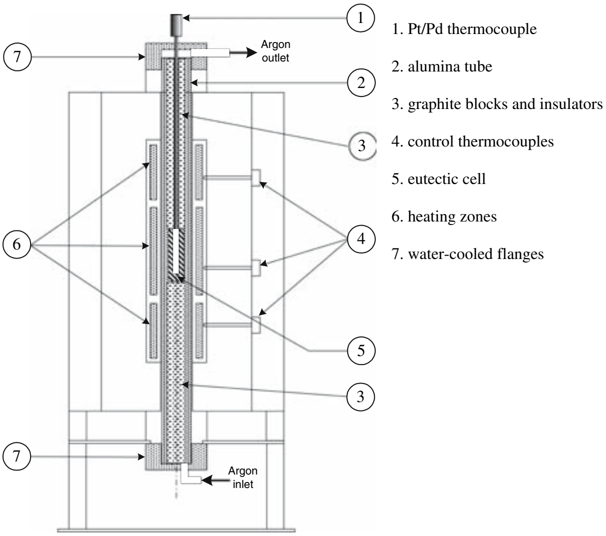

Fig. 2 New LNE high-temperature furnace for high-temperature fixed points operation up to 1,500°C

3.2.2 PTB Furnace Arrangement

The high-temperature furnace of PTB (HTF-R) [6,12] can be used up to temperatures of about 2,300°C. Different atmospheres (argon and hydrogen) and vacuum conditions can be realized. Temperature control is performed by using various thermocouples or a pyrometer. At the top of the furnace, a central pipe-fitting allows the insertion of contact thermometers for calibration. A lateral pipe-fitting with a removable quartz-glass window allows horizontal measurements by means of a pyrometer. The graphite-based heating system consists of a vertical main heater (length: 340 mm) and an auxiliary top heater. Both heaters operate with a direct current to reduce electrical interference during the calibration of thermocouples. Together with special insulation measures, the temperature homogeneity along a eutectic fixed-point cell is better than ±1 K.

A melting and freezing curve of a Co–C eutectic measured by means of the Pt/Pd thermocouple Pt/Pd-PTB-01/06, constructed in the framework of this EUROMET project, is shown in Fig. 3.

3.2.3 NPL Furnace Arrangement

The high-temperature furnace at NPL for metal–carbon fixed points is a vertical three-zone furnace supplied by Carbolite, with a maximum temperature of 1,600°C. The heater elements consist of three Kanthal™ elements made of silicon carbide extending over the entire length of the furnace, interspersed with six shorter elements, three at each end, which constitute the end zones. These zones provide good uniformity along a central high-purity recrystallized-alumina worktube, closed at one end, outer diameter of 75 mm, inner diameter of 65 mm, length of 750 mm, which contains the crucible arrangement. The alumina worktube is equipped with a steel flange at the top,

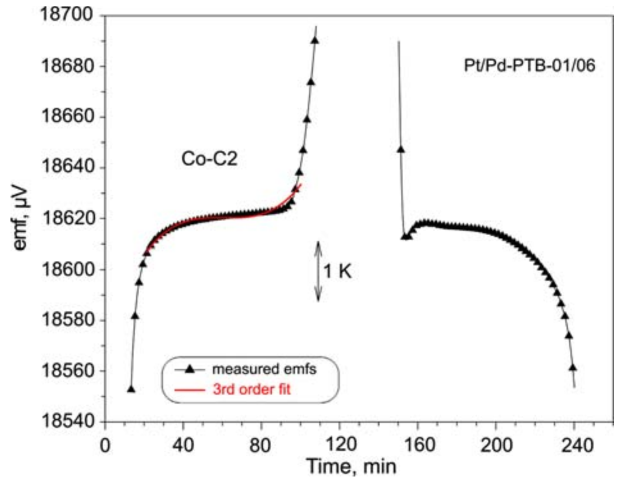

Fig. 3 Typical melt and freeze observed at PTB

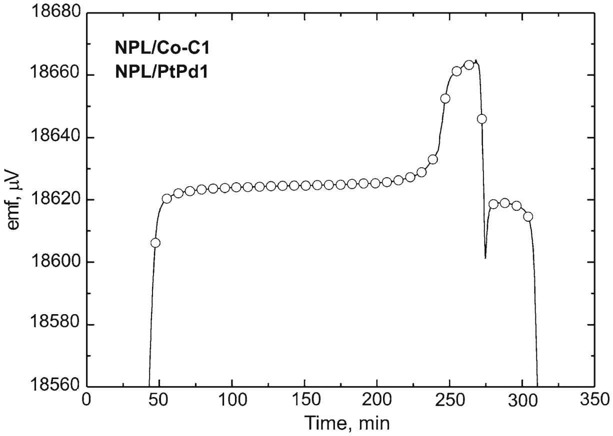

Fig. 4 Typical melt and 'fast' freeze observed at NPL

sealed with a rubber gasket. The flange has a centrally mounted sealed gland to allow entry of a thermocouple while maintaining a gas-tight environment. The worktube is continuously purged with argon gas to maintain a pressure of 1.1 bar. The crucible is enclosed within a hollow graphite cylinder, but mechanically isolated from it, to ensure the lowest possible temperature gradient along the axis [16]. The hollow cylinder is mounted on an alumina brick which sits on the bottom of the worktube. Outside the cylinder, the temperature gradient over the crucible length is approximately 0.5°C at 1,324°C. Stacked on top of the alumina brick are disks of graphite-felt insulation, interspersed with solid graphite disks with a central hole that contact the worktube on the outside, and a thin-walled alumina thermocouple guide tube on the inside, to ensure adequate thermalization of the thermocouple. A typical melt and 'fast' freeze is shown in Fig. 4.

3.3 Platinum/Palladium Thermocouples

Only brief details of the Pt/Pd thermocouples developed for this project are given here as the detailed investigations and results from the participating laboratories are reported in a separate paper [17].

Each participating laboratory has constructed at least three Pt/Pd thermocouples. The Pt and Pd wires were supplied by Alfa Aesar, except for two thermocouples whose wires were supplied by Engelhard-CLAL. Thermocouples were prepared using an agreed procedure, with identical wire and alumina twin-bore insulation dimensions. Experimental parameters that could influence the performance of Pt/Pd thermocouples were investigated. Different measuring junction designs were prepared and the effect of annealing on thermocouple stability and homogeneity was assessed.

The emfs measured at the freezing point of silver for the Pt/Pd thermocouples constructed with wires supplied by Alfa Aesar were very close to the published reference function. It was found that, for some of the thermocouples, the thermoelectric stability and homogeneity was within 50 mK. The different measuring junctions had no significant influence on their thermoelectric performances.

The best thermocouple will be selected to perform the comparison measurements of different Co–C eutectic cells according to the schedule given above.

4 Conclusion and Prospects

A description of the Euromet Project 857, involving three major European national metrology institutes, has been given and early results reported.

This project's outcome will be an important milestone in finding a solution to the problem of calibrating thermocouples at high temperatures with low uncertainties and the associated dissemination to industry. It seems clear that the solution lies in robust high-temperature fixed points used in conjunction with Pt/Pd thermocouples between the freezing point of silver (962°C) and 1,500°C.

Good temperature control of an industrial process is essential for constant quality of manufactured goods, reduced waste, and energy savings. Therefore, the absence of a robust calibration method for contact thermometers above 1000°C has become a significant problem with increasing industrial demand [18,19]. The outcomes of this project will serve these identified and future industrial requirements.

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