Development of an Fe-C Eutectic Fixed-Point for the Calibration and *In-Situ* Monitoring of Thermocouples

G. Failleau [1], T. Deuzé [1], C.J. Elliott [2], J.V. Pearce [2], G. Machin [2], S. Briaudeau [1] and M. Sadli [1]
[1] Laboratoire Commun de Métrologie LNE-Cnam, Paris, France
[2] National Physical Laboratory (NPL), Teddington, United Kingdom
E-mail (corresponding author): guillaume.failleau@lne.fr

Abstract – LNE-Cnam and NPL are involved in a European joint research project (ENG08 *MetroFission*) with the aim of developing new solutions for temperature measurements adapted to the next generation of nuclear power plants, among other applications. One of the objectives of this project is to develop a reference point around 1000 °C – 1200 °C which can be used for the monitoring of the stability of thermocouples and for their calibration in nuclear reactors. The Fe-C eutectic fixed-point has been identified as a potential candidate. This paper will describe the first experiments performed by the two laboratories in collaboration to develop this prospective reference point. In particular the metrological characterisation of the Fe-C melting point is fully detailed.

Keywords: Metal-Carbon Eutectic, Fixed-point, Temperature, Thermocouples

1. INTRODUCTION

Recent work has shown the potential of metal-carbon eutectic fixed-points for the calibration of thermocouples [1-3]. In particular, the melting temperature of the cobalt-carbon eutectic (Co-C, 1324 °C) and the palladium-carbon eutectic fixed-points (Pd-C, 1492 °C) are ideally distributed between the freezing point of copper (1084.62 °C) and the upper limit of use of the Pt/Pd thermocouple (1500 °C), which is considered to be the best contact sensor for accurate measurements in this temperature range.

In the frame of the joint research project (JRP) ENG08 *MetroFission*, LNE-Cnam and NPL are involved in the firt workpackage WP1 (with Centro Español de Metrologia) for developing temperature measurement solutions in the range 1000 °C – 1200 °C, specifically for the next generation of nuclear power plants.

The first step in these developments is the construction and the characterisation of the Fe-C eutectic fixed-point in order to evaluate its ability to be implemented as a temperature reference and/or as a means for monitoring the stability of thermocouples. Copper and Co-C points, which are very close in terms of melting temperature levels and would represent alternative candidates, are not appropriate due to their susceptibility to transmute under ionising radiation.

On the other hand, iron is more stable under neutron irradiation. This is likely to make the Fe-C point particularly suitable for the nuclear industry. Thus, this alloy shows a certain advantage to monitor the long-term stability for in-situ thermocouples under irradiation.

Each of the two laboratories has built a Fe-C cell, with its own crucibles and materials. As a first step for this collaborative work, a comparison was performed with the aim of associating a temperature and a related uncertainty to the phase transition of the constructed cells.

The first results are very promising in terms of repeatability and reproducibility (both less than 1.5 µV (~0.14 °C)) and qualify the Fe-C as a potential fixed-point.

The purpose of this paper is to introduce some new results, obtained after supplementary experiments to characterise this prospective fixed-point, particularly with two specific thermocouples: standard Pt/Pd thermocouples (used by metrology institutes) and type S thermocouples (commonly used in industry). These have both been calibrated, to allow observed temperatures to be estimated.

2. FIXED-POINT CELLS

2.1. Cell assembly

Two cells were prepared and studied independently. The NPL cell was prepared using entirely NPL-sourced materials (iron powder from Alfa Aesar Company®, 99.998% purity, spherical particles; graphite powder from Alfa Aesar Company®, 99.9999% purity, spherical particles). The LNE-Cnam cell was prepared with entirely LNE-Cnam-sourced materials (iron powder from Goodfellow®, 99.99+% purity, spongeous particles; graphite powder from Alfa Aesar Company®, 99.9995% purity, spherical particles). The comparison of further cells, produced cooperatively by sharing materials between the two institutes, thus forming a combination devoted to a thorough investigation of the practical differences between the cells, will be reported in a separate letter. The LNE-Cnam and NPL crucibles are of the same design, but were sourced separately from SGL Group. The graphite grade for NPL crucibles was R6300, whereas the graphite grade for LNE-Cnam crucibles was R6650. Significant differences can be found by comparing the material properties: the LNE-Cnam graphite is both harder and has a greater thermal expansion than the graphite used by NPL. The thermal expansion coefficient quoted by the manufacturer is given to be 5.0 x 10^{-6} K^{-1} and 3.8 x 10^{-6} K^{-1}, respectively. These two parameters may be of importance for the robustness of the cells. Table 1 summarises the cell characteristics.

Cell	Crucible graphite grade	Iron Purity	Initial C Concentration (wt%)
NPL	6300	4N8	3.01
LNE-Cnam	6650	4N+	4.06

Table 1. Fe-C cell characteristics

3. FIXED-POINT CHARACTERISATION

Before performing measurements at the Fe-C fixed-point, each thermocouple is profiled over 10 cm in a silver fixed-point cell to determine the effect of inhomogeneities. The freezing point (961.78 °C) is measured when the thermocouple is fully immersed into the cell and at 1 cm intervals to 10 cm, to measure the maximum difference in the recorded *emf* due to the inhomogeneity of the thermoelements. The value obtained is a component taken into account in the uncertainty budget, with a sensitivity coefficient equal to one.

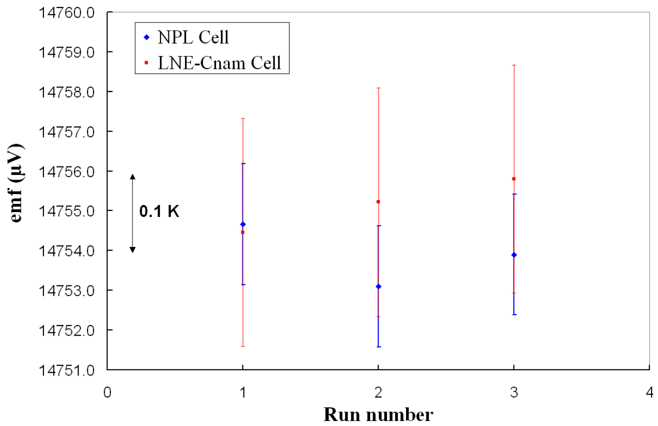

Figure. 1. Fe-C melting and freezing points measured with LNE-Cnam and NPL Pt/Pd thermocouples in the NPL cell at NPL in the one hand, and into LNE-Cnam cell at LNE-Cnam on the other hand. Error bars indicate the expanded uncertainty of the LNE-Cnam (2.80 µV, k=2) and NPL (1.52 µV, k=2) thermocouples.

There is a significant difference between the expanded uncertainties associated with each thermocouple; found to be 2.83 µV (1.52 µV) for the LNE-Cnam (NPL) PtPd thermocouple, and shown in Figure 1. The sensitivity of both Pt/Pd thermocouple is assumed to be 22 µV/°C. In addition, a type S thermocouple was used at LNE-Cnam. This was found upon comparison calibration at 1150 °C, to lie within the standard tolerance of 1.0 °C and has a standard sensitivity of approximately 11 µV/°C.

3.1. LNE-Cnam Cell Construction

The iron and graphite powders used to fill the internal crucible of the LNE-Cnam cell were mixed with a total amount as 141.14 g ± 0.05 g of pure iron and 5.73 g ± 0.05 g of graphite. The carbon concentration in the mixture is therefore estimated to be 4.06 wt%, just below the eutectic concentration (4.3 wt%). The mass of the crucible (m) was measured before and after filling (m_{before} = 150.01 g) and after (m_{after} = 295.49 g), which means a total amount of ingot material, m_{alloy} = 145.48 ± 0.05 g.

3.2. Thermal effects

Melting/freezing cycles were performed by adjusting the upper and lower temperature set points of the furnace to three different offset levels with respect to the melting temperature previously measured (where i K / +j K, where i and j are the furnace offset values before and after the melt). The heating and cooling rates were both 5 K/min.
Figure 2 shows three consecutive melting/freezing cycles obtained with a type S thermocouple within LNE-Cnam cell described above. The reproducibility of the melting plateau, estimated by comparing measurements on different days, was less than 0.55 µV (~ 0.05 °C). Consecutive plateaus within one day were repeatable to the level of 0.32 µV (~ 0.03 °C).
These experiments form a study of the melting process, to shed light on any possible effect on the observed melting point.

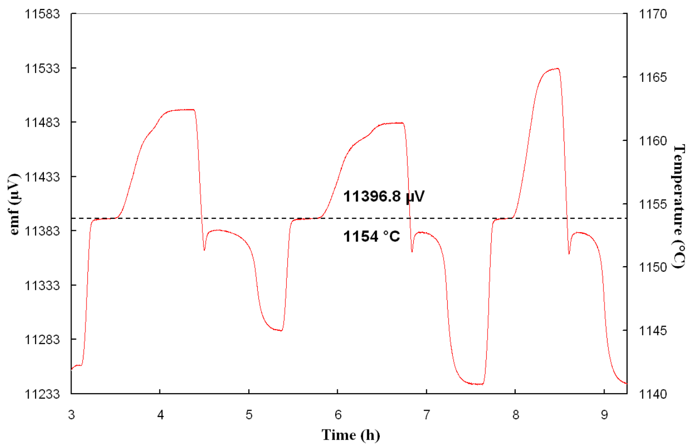

Figure. 2. Melting transition plateaus (red) measured by standard type S thermocouple within the LNE-Cnam cell for three furnace-offset levels at LNE-Cnam. Temperature second derivative curves (blue) allowed us to detect the inflection point.

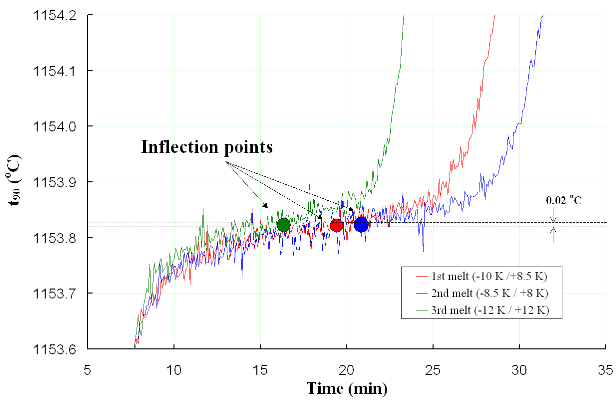

Figure. 3. Influence of the furnace offset on the temperature measured at the inflection point of the melting plateau, measured with the LNE-Cnam Pt/Pd thermocouple and cell at LNE-Cnam.

By superimposing the three melting curves shown in Figure 2, as shown in Figure 3, we find a distribution of points over a scattering domain of the detected inflection points about 0.27 µV (0.02 °C).
Compared to the combined uncertainty given for a CEI 584-1-compliant Type S thermocouple (±1.0 °C, *k* = 2), it can be concluded that no significant influence of the furnace set point temperature is shown by these measurements.

3.3. Fixed-point stability

Another series of measurements consisted of the realisation of melting/freezing cycles with constant furnace conditions, i = j = 12 K.
Figure 4 summarises the results obtained after realising 14 full melting/freezing cycles. We present measurements performed on the same cell, with the LNE-Cnam standard Pt/Pd and S type thermocouples. A maximum deviation of 1.5 µV (0.14 °C) was observed through the whole set of measurements with the type S thermocouple. Moreover three points obtained with the standard Pt/Pd thermocouple clearly show an excellent agreement; less than 1.0 µV (~0.10 °C) with the results obtained with the type S thermocouple, which is calibrated by comparison to the LNE-Cnam standards at 1150 °C. The deviation to the CEI 584-1 norm is measured, allowing the conversion into temperature. The Pt/Pd thermocouple was calibrated at the ITS-90 fixed-points (tin, aluminium and silver) and the cobalt-carbon point. Thus, we were able to extrapolate its response at the Fe-C point in terms of temperature and uncertainties.

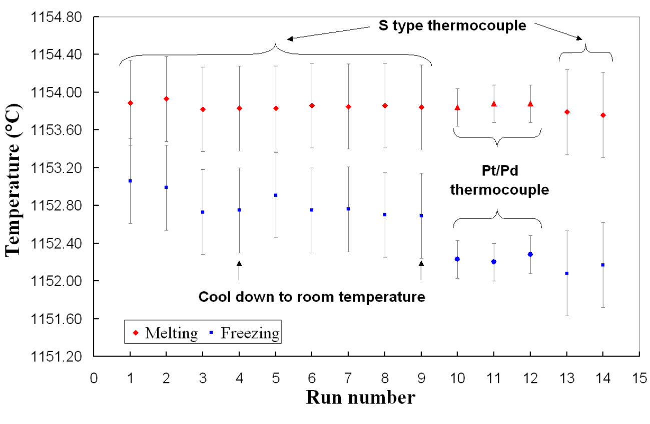

Figure. 4. Fe-C fixed-point stability and temperature comparison recorded with both the LNE-Cnam standard type S and Pt/Pd thermocouples in the LNE-Cnam cell at LNE-Cnam (1 °C for type S and 0.17 °C for Pt/Pd at *k*=2).

Although the melting point is repeatable to a few hundredths of a kelvin, the freezing point seems to be much less repeatable. A noticeable drift is observed along the successive cycles performed confirming earlier results on Fe-C [4]. A systematic deviation (about 1°C for the ten first points, 1.2 °C for the last five) is observed between melting and freezing temperatures, independently on the thermocouple used for the measurements. Similar observations were made with other metal-carbon eutectic points with however less important differences between melt and freeze.
Moreover, it has been noticed that the freezing temperature measured after cooling the furnace to room temperature is slightly higher than the preceding value. These results are in accordance with the work previously published in [5]. This observed behaviour could be explained by a progressive micro structural rearrangement of the alloy following the successive freezing processes [6]. Indeed, it is known that the Fe-C freezing point is highly sensitive to the furnace conditions and the offset applied during the freezing phase transition [7].
The last five measurements are shifted compared to the preceding freezing values, and it is probably due to a change in the furnace configuration (cell has been removed, checked and re-placed). Thus, we cannot conclude yet on a drift induced by the thermocouple (thermal or chemical drift) or by the furnace.
However, it is commonly accepted that the inflection point of the melting plateau represents the reference temperature of the eutectic phase transition. Thus, due to the apparent stability and repeatability of the melting point, we can consider the Fe-C alloy as a convenient candidate fixed-point for the calibration of thermocouples in this range of temperatures.

4. CONCLUSION

Regarding the satisfactory performance of the Fe-C studied in this work, it seems that this alloy is very promising for calibration. The melting temperature (~1153 °C) fits perfectly with the maximum temperature range expected into the next generation of nuclear reactors (1000 °C – 1200 °C). Moreover, the Fe-C cell constructed and studied at LNE-Cnam presents a good reproducibility and repeatability better than 1.0 µV (~0.1 °C) observed at the melting point.
These first results allow us to consider the Fe-C melting point as an interesting temperature reference, suitable for further developments as a part of *in-situ* self-validating devices.
Nevertheless, although the performances in terms of fixed-point temperature measurement are very promising, some difficulties have been encountered with Fe-C cell regarding their robustness. Indeed, some breakages are observed on the external crucible wall (as it is described by F. Edler in [4]). The most probable explanation is that the cells are subject to a high internal stress due to large volume expansion of the ingot upon transformation into the liquid phase. Of course, temperature profiles inside the furnaces used are always checked and tuned before each series of measurements, but it will be necessary to investigate the reasons of the observed robustness issues. An important consideration is the crucible material properties such as its elastic constant, young modulus and thermal expansion coefficient. In this work, the NPL cell (constructed with R6300 graphite grade) was broken on the outer wall but in contrast, the LNE-Cnam cell (constructed with the R6650

graphite grade) remained intact despite 20 melting/freezing cycles. A further investigation will be presented in a future paper.

5. ONGOING WORK AND PROSPECTS

Thermocouples drift significantly in use, both due to the thermal environment and, in a nuclear power plant, due to continuous irradiation. The aimed output of this work, started with Fe-C fixed-point development, will be to demonstrate the practicality of self-validation methods for specific thermocouples. Indeed, conventional thermocouples (type K, for instance) have a maximum working temperature around 1100 °C and transmute under ionizing radiation. The Mo/Nb thermocouple family offers an interesting alternative, especially for the next generation of power plants: they exhibit a low neutron cross section and can bear much higher temperatures [9]. In the frame of ENG08 *MetroFission* JRP an investigation is planned, where the metrological characteristics of these sensors and the means for enhancing their stability and ensuring their traceability will be studied.

Through this work, it will be possible to propose innovative devices, allowing the self-validation of sensors [10] to be implemented into nuclear reactors or other industries which require monitoring of temperatures around 1150 °C, as instrumented by small sized Fe-C fixed-points.

REFERENCES

[1] J.V. Pearce, V. Montag, D. Lowe, W. Dong: "Melting temperature of high-temperature fixed points for thermocouple calibrations"; *Int. J. Thermophys. Vol.32, pp463-470, 2011*.

[2] H. Ogura, M. Izuchi, M. Arai: "Evaluation of a cobalt-carbon and palladium-carbon eutectic point cells for thermocouple calibration"; *Int. J. Thermophys.,*Vol.29, 2008, pp. 210-221.

[3] E.R. Woolliams, G. Machin, D.H. Lowe, R. Winkler: "Metal (carbide)–carbon eutectics for thermometry and radiometry: a review of the first seven years"; *Metrologia.,* Vol.43, 2006, R11-R25.

[4] F. Edler, A.C. Baratto: "Comparison of nickel-carbon and iron-carbon eutectic fixed-point cells for the calibration of thermocouples"; *Metrologia*, Vol.43, 2006, pp. 501-507.

[5] I. Yang, Y.-G. Kim, K.S. Gam: "The dependence of the melting temperatures of the eutectics Fe–C and Co–C, designed for thermocouple thermometry, on the furnace offset temperature during the preceding freeze"; *Meas. Sci. Technol.*, Vol.19, 2008, 015106.

[6] Z. Wei, P. Bloembergen, Y. Yamada, Y. Wang, W. Tao: "The dependence of the structure of eutectic Fe-C on freezing and annealing conditions and on the impurity content"; *Acta Metrologica Sinica*, Vol.5A, 2008, pp. 109-115.

[7] P. Bloembergen, Y. Yamada, N. Sasajima, Y. Wang, T. Wang, "The effect of the eutectic structure and the residual effect of impurities on the uncertainty in the eutectic temperatures of Fe–C and Co–C "; *Metrologia.* Vol.44, 2007, pp. 279-293.

[8] D. Lowe, K. Mingard, Z. Malik, P. Quested: "The dependence of the melting temperature of cobalt-carbon eutectic on the morphology on its microstructure"; *Int. J. Thermophys*, Vol.28, 2007, pp. 2019-2027.

[9] J.F. Villard, S. Fourrez, D. Fourmentel, A. Legrand: "Improving high temperature measurements in nuclear reactors with Mo/Nb thermocouples"; *Int. J. Thermophys*, Vol.29, 2008, pp. 1848-1857.

[10] O. Ongrai, J.V. Pearce, G. Machin, S.J. Sweeney: "Miniature Co-C eutectic fixed-point cells for self-validating thermocouples"; *Meas. Sci. Technol.* Vol.22, 2011, 015104.

Author (s):

Dr., Guillaume Failleau, Laboratoire Commun de Métrologie LNE-Cnam, (1 rue Gaston Boissier, 75724 Paris Cedex 15, France), phone: +33130691139, fax number: +33130691234, guillaume.failleau@lne.fr

Thierry Deuzé, Laboratoire Commun de Métrologie LNE-Cnam, (1 rue Gaston Boissier, 75724 Paris Cedex 15, France), phone : +33130693970, fax number: +33130691234, thierry.deuze@lne.fr

Dr., Claire Elliott, National Physical Laboratory, (Hampton Road, Teddington, United Kingdom TW11 0LW), phone: +442089436832, claire.elliott@npl.co.uk

Dr., Jonathan Pearce, National Physical Laboratory, (Hampton Road, Teddington, United Kingdom TW11 0LW), phone: +442089436886, jonathan.pearce@npl.co.uk

Pr., Graham Machin, National Physical Laboratory, (Hampton Road, Teddington, United Kingdom TW11 0LW), phone: +442089436742, graham.machin@npl.co.uk

Dr., Stephan Briaudeau, Laboratoire Commun de Métrologie LNE-Cnam, (61 rue du Landy, 93210 Saint-Denis La Plaine, France), phone: +33158808927, fax number: +33158808900, stephan.briaudeau@cnam.fr

Dr., Mohamed Sadli, Laboratoire Commun de Métrologie LNE-Cnam, (61 rue du Landy, 93210 Saint-Denis La Plaine, France), phone: +33140272023, fax number: +33158808900, mohamed.sadli@cnam.fr