Developments around the Co-C eutectic point at LNE-INM/Cnam

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Abstract: Like many other NMIs, LNE-INM/Cnam has concentrated its high-temperature activities around the realisation and characterisation of metal-carbon eutectic points, parallel with the radiometric temperature measurements at the highest temperatures. In this paper will be described the work accomplished around the Co-C eutectic point during the last months in order to improve the robustness of the cells and the quality of the plateaux. New cell design and filling technique, allowing to fill a cell in one step with minimised risks of contamination, have been developed and will be described. The results obtained with cells filled by different methods will be presented.

Key words: Fixed point, Metal-Carbon eutectics, Temperature uniformity, High temperatures

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1. Introduction

At the start of the European project HIMERT [1], the first metal-carbon eutectic cells were constructed at LNE-INM/Cnam with the following procedure[2]: the eutectic mixture was, beforehand, prepared under argon atmosphere by mixing pure powders of graphite and metal. The proportion of graphite was usually chosen about 1% below the eutectic composition [3], the remaining proportion of graphite being provided by the crucible during the melt. The cell was filled with the mixture to the top then cycled in the furnace reaching the melting temperature. This last step was reiterated around about ten times until the cell was filled, as the volume after melting was lower than the prepared powder.

This first filling method had to be improved as the difference of expansion between the metal and the graphite of the crucible often caused breakage of the external part of the cell. This problem was solved by placing a loose sleeve in the crucible. This sleeve separates the ingot from the outer wall of the crucible and could break without damaging the cell. The number of fillings had also to be limited to reduce the contamination of the cell and improve the homogeneity of the eutectic. It has been cut down at about five steps by screwing a funnel on top of the crucible allowing to pour the mixture above the top of the cell. This design was working but some cells broke when the mixture stuck to the funnel during the last fillings. The cavity was then pulled by the metal shrunk to the funnel during the cooling process. This problem has been partly resolved with a fourth design and filling process. A piston was added to the funnel in order to push down the metal during the melt[4]. Despite the first difficulties to implement the process, this new filling method presented many advantages which are described below; the latest cell and filling parts design includes this procedure.

2. A sleeve or C/C sheets?

A few years ago, NMIJ proposed the usage of a graphite fabric (C/C sheets) inside the crucible, around the

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eutectic ingot with the two following advantages: the temperature uniformity around the ingot was considerably improved allowing longest and flattest plateaux, and the difference of thermal expansion between the crucible and the ingot seemed to be solved by the C/C sheets[5].

The Co-C cells constructed by LNE-INM in the frame of the long-term stability study and the CCT-WG5-coordinated international project on high-temperature fixed-points[6] used C/C sheets but unfortunately, only three out of the four cells required have been filled due to more breakage problems than those we had with the sleeve design. On the other hand, other national institutes observed the same problems of breakage mainly on Co-C cells. NMIJ has also recently showed, on two of their Co-C cells using C/C sheets that the duration of the plateaux has decreased considerably after a certain time of usage[7]. This effect seems to be due to the lack of metal around the cavity after the C/C sheets had been damaged by the metal.

Despite the fact that LNE-INM has successfully filled three Co-C cells with C/C sheets showing relatively flat and long plateaux, this drawing seemed inefficient for Co-C and more suitable for Re-C and Pt-C points. The Co-C seems to show the worst robustness of the three eutectics probably mainly because of its thermal expansion. The difference of expansion can be calculated using equation 1, where l_0 is the length of a sample at room temperature; l, the length of the sample at a given temperature; θ, the difference of both temperatures and a, the coefficient of thermal expansion of the sample.

$$l = l_0(1 + a\theta) \qquad (1)$$

Tab. 1 Difference of expansion between the graphite R4550 and the eutectics Co-C, Pt-C and Re-C from room temperature to the melt. The induced mechanical stresses on a Co-C cell are about twice those applied on a Re-C cell.

Metal carbon eutectic	**Co-C**	**Pt-C**	**Re-C**
Coefficient of thermal expansion (10e-6/K)	12,5	9	6,6
Difference of temperature from 23癈 to the melt (K)	1302	1715	2451
Expansion of the eutectic along a 3 cm length cavity (mm)	**0,33**	**0,26**	**0,19**

Table 1 shows the difference of expansion from room temperature to the melting temperatures between the graphite grade R4550 (a = 4.10^{-6} K^{-1}) and the three metal-carbon eutectics Co-C, Pt-C and Re-C.

Last year, not less than fifteen Co-C cells were constructed with five different types of graphite (R4550, R4340, Ringsdorff, Poco SFG-2 and ATJ 49) in order to construct four cells in the frame of the WP1, confirm the one-step filling process with the piston and study the effects of the thermal expansion. Table 2 shows the number of broken cells during and after filling for each group of cells.

Tab. 2 Number of broken cells during and after filling for further grades of graphite.

Graphite	ATJ49	R4340	R4550	Ringsdorff	Poco SFG-2
Coef. of thermal expansion [7] (10e-6/K)	2,5	2,9	4,0	5,1	8,1
Number of cells filled	1	2	5	4	3
Number of broken cells during filling	0	1	3	2	3
Number of broken cells after implementation	0	1	2	2	–

Four main conclusions can be drawn from this study:

- a particular attention must be given to the robustness of the eutectic cells, especially during the filling process,
- the robustness of the cells seems to be not directly dependant on the thermal expansion of the graphite. In other terms, the graphite with the thermal expansion close to the metal is not a guaranty of success,
- the sleeve improves the robustness of the cell,
- during the filling and the implementation of the cells, the cooling rate should be smaller than 700°C/h.

Following these conclusions, a new cell design was developed last year at LNE-INM. This design keeps the advantages of the one-step filling with the piston, the presence of a sleeve for its ability to improve the robustness, and still one C/C sheet for the temperature uniformity inside the cell. It has been tested at the end of 2007 on a copper cell which showed excellent results: plateaux of more than 30 minutes with only 30 g of copper. Since then, 6 Co-C cells have been filled, to date, and none of them has broken during filling. Four of the cells have been recently sent to NMIJ for studying their long term stability in the frame of WP1 of the international project on high-temperature fixed points. So, the answer to the question in the title of this section, at least for the moment and as far as LNE-INM is concerned, is: both!

2. Double structure cell design

This new design (figure 1) is similar to the sleeve drawing with a free space left between the crucible and the sleeve to insert a C/C sheet. The funnel is screwed on the crucible allowing to fill the whole cell in only one step. It also guides the piston to push on it when the mixture melts.

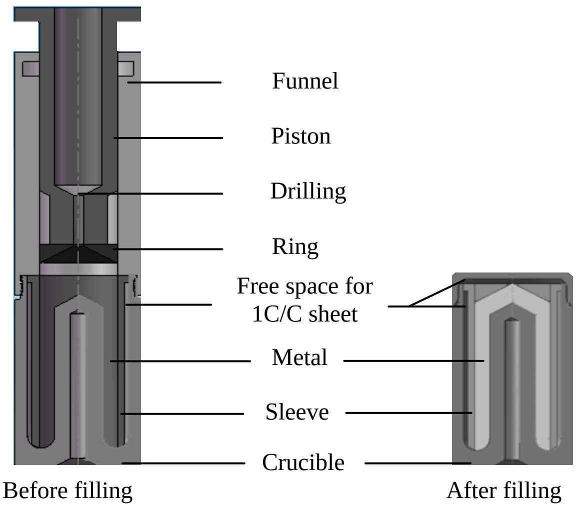

Fig. 1 New cell design. A C/C sheet is wrapped between the crucible and the sleeve. The funnel is screwed to the crucible. The piston and the ring can move on the vertical axis.

Instead of the C/C sheets, the sleeve, directly in contact with the eutectic, can provide the lack of graphite to reach the eutectic composition during the melt without being too much damaged. The inner volume remains thus unchanged when the cell is aged. The C/C sheet, close to the ingot but not in contact with it, continues to behave as a thermal screen being now protected by the sleeve.

3. Filling process

All parts of the crucible and filling pieces are first cleaned in two ultrasonic-baths of alcohol and bi-distillated-water and baked during half an hour in the Vega HTBB 3200pg[8] furnace at 2000 K. The cell is then assembled by placing the C/C sheet and the sleeve inside the crucible and screwing the funnel. The whole mixture is poured until the cell is filled. A few extra grams of the mixture are added in order to be sure that the cell is completely filled and to obtain a sample for analysis at the end of the filling. All the cells were filled with the same mixture containing ~2.4 % of graphite, with the same grade of cobalt and graphite. The cells were filled with the same process in one step except 2Co2, filled in two. The ring and the piston are then placed inside the funnel. All these operations are made under argon atmosphere in a glove box.

The cell is then placed in the HTBB furnace, set up in the vertical position. A rod, of about 20 cm length (not represented in fig.1), is screwed on the piston. The set point of the furnace is chosen only ~20 °C above the melting point in order not to let too much graphite saturate the mixture. When the melt occurs, the rod (screwed to the piston) sinks in the funnel until the totality of the mixture melts. The liquid can then rise inside the piston by the drilling by applying a light pressure on the rod. When the piston is stopped by the funnel, the ring covers exactly the top of the cell; the furnace is then brought down gently to room temperature (maximum cooling rate of about 700 °C/h).

The funnel can be removed from the crucible by spinning the piston in order to cut the metal at the top of the ring; the funnel can then be unscrewed. The cell is ready after placing a C/C disk on its top and screwing the cap. At LNE-INM, 6 cells machined in R4550 have been successfully filled with this process with the following advantages:

- By reducing the number of filling, the purity of the metal is conserved as well as possible.

The homogeneity of the mixture is probably better than a multi-step filling where the first layers are more often supplied by the graphite from the crucible.

- The crucibles can be filled with a good reproducibility. The masses of the 6 cells, identical within 3%, show that the volumes of the ingots are quasi-similar.
- The ring does not allow the mixture to move, especially near the bottom of the cavity, where the shape of the ingot may have a straight effect on the plateaus.
- The cells can be filled with a proportion of graphite close to the eutectic, allowing to reduce the proportion of graphite provided by the sleeve thus to improve the robustness and the cell stability.
- The melting temperature is known, without any measurement, by the motion of the piston.
- After filling, the remaining quantity of eutectic inside the piston can be used as a sample to be analysed.
- A Co-C cell can be filled in only one day. Seven days were necessary to fill the 6 cells, including their cleaning, in the HTBB.
- None of the 6 cells has broken during the filling or after the first implementation.

4. Temperature uniformity of the HTBB

The melting temperature of the metal-carbon eutectics is strongly dependant on the temperature uniformity of the furnace[8-10]. Despite the fact that the HTBB 3200pg is a single zone furnace, its temperature distribution can be adjusted by ordering the rings of the heater[11,12]. This one consists of about fifty pyrolitic graphite rings compressed between two electrodes. After the measurement of their electrical resistivity, the temperature uniformity can be improved by putting the most resistant rings at the extremities of the heater. At LNE-INM, the measurement of the temperature distribution is made directly inside the cell holder with the a pyrometer tilted by about 4.5° from the furnace axis (fig. 3).

This type of cell holder has been designed to fill two functions. The first one is to measure the temperature distribution the closest to the cell and not directly on the rings of the heater. The second one is to install the cell inside the cell holder without dismounting the furnace in order not to alter the contacts between the rings. Figure 4 shows the temperature distribution of the HTBB 3200pg at 1600 K (corresponding to the Co-C melting point) before and after different ring arrangements.

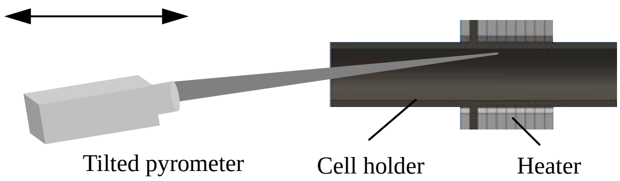

Fig. 3 Measurement of the temperature distribution inside the cell holder (cross section) with the tilted pyrometer.

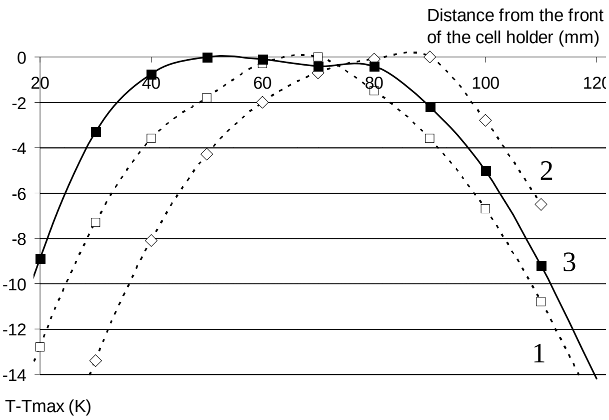

Fig. 4 HTBB 3200pg temperature distribution at the Co-C melting point, before (curves 1 and 2) and after improvement (curve 3). The cell can be located in a temperature gradient better than 1 K over 40 mm.

5. Results

5.1 First plateaux of the new cells

The double-structure cells 2Co2, 2Co3, 2Co4, 2Co5, 2Co6 and 2Co7 have been implemented in the HTBB 3200pg with a melt set-point of about 20 K above the melting temperature in a temperature distribution of 4 °C along the 40 mm length of the cell (corresponding to curve 1 in fig. 4). For each cell, 3 plateaux have been measured within a day. The melting temperatures obtained with all cells in this “bad” temperature distribution range within about 0.1 K.

One of these cells, 2Co7, has been studied more thoroughly and implemented during four days. Figure 5 shows the 11 melting temperatures of 2Co7 implemented in the HTBB 3200pg with different set-point levels (±15 K, ±20 K and ±25 K). Oppositely to the 3 first plateaux, the 8 last melting points have been performed after the improvement of the temperature uniformity (curve 3, figure 4). The temperatures have been measured at the inflection point of the plateaux measured with the LP5 pyrometer (not calibrated).

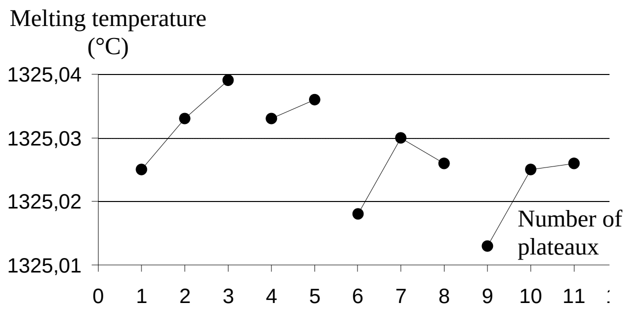

Figure 5: Reproducibility of the melting temperatures of the eutectic Co-C cell 2Co7 measured with the LP5 pyrometer (not calibrated). The measurements performed the same day are linked by lines.

The eleven melting temperatures lie within less than 30 mK. This good repeatability includes the first plateau of each day of implementation, usually not taken in consideration, due to its lowest temperature.

5.2 Comparison between double-structure and C/C sheet-type cells

The longest and flattest plateau of Co22, a cell with C/C sheets, has been compared with the plateaux of the double-structure cells 2Co2 and 2Co7 described in §5.1 (Fig.5). Co22 was filled in two steps, with the same proportion of graphite, the same purity of cobalt and the same process as the double-structure cells. The three cells were studied in a temperature step of -15 K /+15 K around the melting point.

The duration of the plateaux obtained with the double-structure cells are a bit shorter than the previous design but the slopes are flatter (respectively 25 mK/300s against 30 mK/300s). These differences can be explained by a loss of efficiency of the thermal shield of the double-structure cells due to the reduction of the number of C/C sheet (1 in a double-structure cell instead of 3). However, the recent improvement of the temperature uniformity of the HTBB 3200pg (among other furnaces) allows to extend the duration of the plateaux by reducing the temperature step (chosen at the beginning of the HIMERT project from 15 K to 30 K in order not to be affected by the bad temperature uniformity of the furnaces).

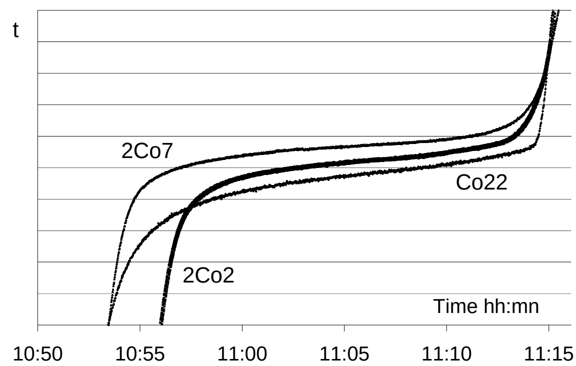

Fig.6 Comparison between the best plateau of Co22 filled with the previous cell design (C/C sheet) with the first plateaux of the new double-structure cells. On the vertical axis, one indentation corresponds to about 0.1 K.

6. Conclusion

The thermal expansion of the Co is suspected to have caused many Co-C cell breakages. Adapting the thermal expansion of the graphite constituting the crucible to that of the metal is not a guaranty of success. The heating and cooling rates applied are strongly linked to the breakage of the cell. To be on the safe side, they must not exceed respectively 1000°C/h and 700°C/h all along the filling process

Cells with C/C sheets showed many advantages as the flatness or the length of the plateaux but the robustness and the long term stability seems to be reduced by the C/C sheets. In order to conserve the advantages of the C/C sheets and preserve the robustness provided by the previous drawing with the sleeve, a double-structure cell was developed, joining the advantages of both designs. The first double-structure cell, filled with high-purity Cu, showed a stability within 3 mK during 30 mn when placed in a 3-zones furnace in a temperature uniformity of 0.5 K. The six following Co-C cells recently filled (2Co2 to 2Co7) showed promising results as described in this paper. Four of them were sent to NMIJ to be aged in the frame of the WP1 of the CCT-WG5 project on high-temperature fixed-points.

The comparison between the best plateaux of the working cells based on the previous cell design (C/C sheets) with the double-structure cells has given comparable results. These results show that the one-step filling process associated to the double-structure design can be a good alternative to the C/C sheet cells. The robustness remains the main problem to solve before studying the long-term stability, but for the first time at LNE-INM/Cnam, 6 Co-C cells filled in the new crucible with the one-step filling method did not break during filling or the first implementations.

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