Construction of a Cr$_3$C$_2$-C Peritectic Point Cell for Thermocouple Calibration

Hideki Ogura*, Thierry Deuze**, Ronan Morice**, Pascal Ridoux***, and Jean-Remy Filtz***

Abstract: The melting points of Cr$_3$C$_2$-C peritectic (1826°C) and Cr$_7$C$_3$-Cr$_3$C$_2$ eutectic (1742°C) alloys as materials for high-temperature fixed point cells are investigated for the use of thermocouple calibration. Pretests are performed to establish a suitable procedure for constructing contact thermometry cells based on such chromium-carbon mixtures. Two cells are constructed following two different possible procedures. The above two melting points are successfully observed for one of these cells using tungsten-rhenium alloy thermocouples.

Key Words: Cr$_3$C$_2$-C peritectic-point, Cr$_7$C$_3$-Cr$_3$C$_2$ eutectic-point, melting plateau, thermocouple calibration.

1. Introduction

In 2004, high-temperature fixed points reported by Yamada et al. in 1999 [1] were investigated by Morice et al. for thermocouple applications up to 2000°C [2]. More recently, Yamada et al. have reported new high-temperature fixed points based on several metal carbide-carbon peritectic points [3]. Phase transitions were observed at the Cr$_3$C$_2$-C peritectic point (1826°C) and Cr$_7$C$_3$-Cr$_3$C$_2$ eutectic point (1742°C) using a radiation thermometer [4],[5]. A repeatability of 20 mK was found at the peritectic point and of 210 mK at the eutectic point using the same cell. Although the eutectic point seems insufficient for use as a primary standard, both eutectic and peritectic points would find application in the study of thermocouples based on W-Re alloys used in this temperature domain, as a low-cost alternative to previous high-temperature fixed points constructed at the Pt-C eutectic point (1738°C) and Ru-C eutectic point (1953°C) [6].

However, difficulties were reported in filling crucibles with chromium-carbon mixtures. The low surface energy of the molten metal and its high viscosity [4] led to the formation of voids within the ingot. Different techniques were tested to improve the fabrication of cells with less than 20 g of alloy, for application to radiation thermometry.

Contact thermometry cells require a larger amount of alloy, typically ten times higher in weight than that for radiation thermometry, and specific fabrication techniques. Good cell filling is essential since the thermocouple may not reach the temperature of the phase transition if the hot junction of thermocouple is surrounded by an ingot with many voids. In this work, different filling methods are tested and two Cr$_3$C$_2$-C peritectic point cells are constructed. A procedure for cell construction using a Cr-C mixture is proposed.

2. Investigation of New Filling Techniques for Cr-C System

The cell (outer diameter: 37 mm; outer length: 124 mm) used is composed of an internal crucible containing a metal and a larger external crucible. Firstly, fabrication usually consists of filling the crucible with the required amount of a metal-carbon mixture. The thermometer well is then inserted in the molten metal. The resulting aspect of the ingot essentially depends on the preparation of the metal. In particular, the presence of voids seems to strongly depend on the shape of the raw materials used to form the ingot [5]. Different filling techniques were tested using small test crucibles, including a method successfully used by Yamada et al. to prevent the formation of voids within the ingot. This technique uses a C/C sheet (a 0.5-mm-thick purified graphite cloth material) as an absorber of molten chromium-carbon mixtures owing to the good wetting properties of this alloy. Several layers of C/C sheets were tightly packed in each test crucible so that the molten metal penetrated every corner of the crucible through the capillary effect.

In this work, the same furnace was used to carry out the tests, and fabricate the cells for their subsequent use. The high-temperature furnace (Fig. 1) used consists of a graphite cylindrical heater insulated with graphite fibres. The assembly is placed in an airtight enclosure, which enables it to operate in vacuum or inert gases. The enclosure is cooled by circulating water. The stability of the furnace between 1000 and 2000°C is better than ±0.1°C over 1 h. The crucibles are set centrally in the furnace.

2.1 Description of Pretests

Sets of small samples were constructed to assess different filling methods before constructing large cells. The small crucibles used for the pretests (see Fig. 2) consisted of a cup-shaped graphite crucible and a graphite cover. Each small crucible was 24 mm in outer diameter and 38 mm in height.

All graphite crucibles were purified in high-purity ethanol using an ultrasonic bath, and then baked at 2000°C for 1 h in vacuum before filling them with chromium shots, carbon powder.

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Chromium was supplied by Alfa Aesar in the form of shots (approximately 5 mm in diameter). The nominal purities of the chromium shots, carbon powder and C/C sheet were 99.999, 99.9999 and >99.999 %, respectively (metal basis).

Data of the five samples shown in Fig. 2 summarize the different tests carried out to assess the different filling methods used. The sample “S-No.1” was constructed using a mixture of chromium shots and carbon powder. The sample “S-No.2” was filled with chromium shots and C/C sheets alternately. The samples “S-No.3” and “S-No.4” were filled with chromium shots mixed with both graphite powder and C/C sheets at approximately the peritectic composition. The C/C sheets contained in S-No.4 had holes at the center except for several sheets at the bottom. The sample “S-No.5” was filled with chromium shots and carbon powder alternately like layers. The weights of chromium shots, carbon powder and C/C sheets are listed in Table 1.

2.2 X-ray Transmission Photographs of Small Samples

After melting, all the small samples were checked using X-ray transmission photographs. These photographs are shown in Fig. 3. White parts indicate metal-rich regions and black parts indicate voids or graphite-rich regions.

Table 1 Weights of Cr shots, C powder and C/C sheets for construction of small samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S-No.1</th>
<th>S-No.2</th>
<th>S-No.3</th>
<th>S-No.4</th>
<th>S-No.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr shot</td>
<td>11.2 g</td>
<td>7.0 g</td>
<td>7.7 g</td>
<td>8.3 g</td>
<td>7.2 g</td>
</tr>
<tr>
<td>C powder</td>
<td>1.5 g</td>
<td>/</td>
<td>0.4 g</td>
<td>0.2 g</td>
<td>1.1 g</td>
</tr>
<tr>
<td>C/C sheet</td>
<td>/</td>
<td>1.1 g</td>
<td>0.8 g</td>
<td>1.0 g</td>
<td>/</td>
</tr>
<tr>
<td>Composition of C (w%)</td>
<td>12 %</td>
<td>14 %</td>
<td>13 %</td>
<td>13 %</td>
<td>13 %</td>
</tr>
</tbody>
</table>

The samples were heated at a rate of 15°C/min in vacuum until the content melted at the peritectic melting point. Furnace temperature was maintained at approximately 20°C above the melting temperature for 20 min to ensure good diffusion of carbon in the molten metal. The furnace was then cooled to room temperature at a rate of 15°C/min.

2.3 SEM Image of Small Sample

After melting, since it was impossible to unfasten the graphite cover from the cup-shaped graphite crucible, S-No.1 was cut above the top of the ingot to check its inner wall. It was found that the inner wall of the crucible was coated with...
chromium metal because of its high vapor pressure. Subsequently, the ingot was cut vertically to observe its inside after removing the graphite crucible using a lathe. During the cutting, the ingot broke into several pieces owing to its fragility. Figure 4 (a) shows one of the pieces immediately after breakage. The right side of the piece was around the removed graphite crucible, while the dark part of the left side was just around the center of the ingot. Figure 4 (b) shows a magnified SEM image of the area around the dark part in Fig. 4 (a). It was found that the center of the ingot contained small voids among many whiskerlike crystals, but there was no large void inside the ingot. The original X-ray transmission photograph of S-No.1 in Fig. 3 shows these voids and crystals. It is considered that these small voids were formed as a result of ingot shrinkage during the freezing. Such a structure, as primarily identified in X-ray images was also observed in other X-ray transmission photographs as further described below.

After SEM, S-No.1 was used for density measurement to determine the weight of the ingot required for the optimal filling of large cells. It was found that the density of S-No.1 was 6.5 g/cm$^3$.

### Table 2: Information on construction of large cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Cr-C-LNE No.1</th>
<th>Cr-C-LNE No.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filling cycle</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Environment</td>
<td>Vacuum</td>
<td>Ar gas</td>
</tr>
<tr>
<td>Weigh of ingot</td>
<td>106 g</td>
<td>100 g</td>
</tr>
<tr>
<td>Composition of carbon (wt%)</td>
<td>13 %</td>
<td>12 %</td>
</tr>
</tbody>
</table>

Fig. 5 X-ray transmission photographs of (a) Cr-C-LNE No.1 and (b) Cr-C-LNE No.2 cells before insertion of thermometer well.

### 3. Construction of Large Cells

Since S-No.5 (without C/C sheet) was found to provide the best results in terms of ingot structure, two large crucibles were filled with chromium shots mixed with graphite powder with no C/C sheet at approximately the peritectic composition. Chromium shots and graphite powder were drawn from the lot used in the pretests. The crucibles (10 ppm of ashes), supplied by SGL Carbon, were purified and baked following the procedure described above. The crucibles and their content were heated and cooled in several steps. The heating rates were 15°C/min up to 1500°C, 10°C/min up to the eutectic point and 5°C/min above the eutectic point. Furnace temperature was maintained at approximately 25°C above the peritectic melting temperature for approximately 1 h. The cooling rates were 5°C/min down to approximately 1000°C and approximately 15°C/min down to room temperature. From some pretests using the small samples, it was found that chromium metal easily vaporizes in vacuum owing to its high vapor pressure; thus, the atmosphere effect was measured during melting. The Cr-C-LNE No.1 cell (named cell No.1 hereafter) was filled in vacuum, whereas the Cr-C-LNE No.2 cell (named cell No.2 hereafter) was filled in Ar gas atmosphere. This process was repeated until the weight of the ingot reached approximately 100 g, which was calculated using the density of S-No.1. Filling was completed in two cycles for cell No.1 and in six cycles for cell No.2. The filling conditions for and resulting overall characteristics of cell Nos.1 and 2 are summarized in Table 2.

Figures 5 (a) and (b) show X-ray transmission photographs of large cells before the insertion of the thermometer well. These photographs show large voids within the ingot of cell No.1, particularly on the top part of the ingot. Complete filling in two cycles was clearly insufficient. Unlike cell No.1, cell No.2 achieved good filling resulting in an ingot structure nearly free of voids.

Subsequently, the thermometer well was inserted into the ingot in the molten state, as shown in Fig. 6. The thermometer
well of cell No.1 was inserted in vacuum, whereas that of cell No.2 was inserted in Ar gas atmosphere. During the insertion of the thermometer well, furnace temperature was maintained at approximately 50°C above the peritectic melting temperature for approximately 1 h. The temperature distribution was ±2°C from the bottom of the cell up to 150 mm.

After melting, it was found that the thermometer well could not be inserted into cell No.1 at full immersion. No such case was encountered for cell No.2, where the thermometer well was always inserted smoothly, even at full immersion. Considering that chromium metal easily vaporizes in vacuum, the inner crucible might have been coated with chromium metal during melting, particularly around the top of the inner crucible. Consequently, a highly viscous chromium coating prevented the smooth penetration of the thermometer well.

Figures 7 (a) and (b) show X-ray transmission photographs after the insertion of the thermometer well. It was clear that large voids still remained after the insertion. Compared with cell No.1, cell No.2 showed an absence of voids in the ingot even after the insertion of the thermometer well, as shown in Figs. 5 (b) and 7 (b). On the other hand, clear stripe patterns can be observed around the top of the ingot in Fig. 7 (b) as well as around the bottom of the ingot in Fig. 5 (b). As described in section 2.3, it is considered that these stripes indicate the presence of the whiskerlike crystal structures shown in Fig. 4 [7].

4. Observation of Melting Plateaux

At this stage, cell No.2 is under investigation. The melting plateaux of cell No.2 at the eutectic and peritectic points obtained from measurements using a type C thermocouple (tungsten-rhenium 5%/tungsten-rhenium 26%) are shown in Figs. 8 (a) and (b). To realize the melting plateaux at the eutectic and peritectic points, the temperature difference between the surrounding temperature and each melting point was 16°C.

It was possible to observe the Cr7C3-Cr3C2 eutectic point and Cr3C2-C peritectic point from cell No.2 using thermocouples.
5. Conclusion

The Cr$_7$C$_3$-Cr$_3$C$_2$ eutectic point and Cr$_3$C$_2$-C peritectic point were investigated for thermocouple calibration as alternatives to the Pt-C and Ru-C eutectic points. Compared with metal-carbon alloys that have been used so far to develop high-temperature fixed points for contact thermometry, crucibles filled with chromium-carbon mixtures at approximately the peritectic composition still require the assessment of specific procedures to avoid the formation of voids within ingots. The successful construction of a first chromium-carbon cell paves a new way for the study of refractory thermocouples.

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[7] Private communication with F. Zielinski, Non-Destructive Testing and Metallurgy Division of LNE.

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