

## SILICON-CARBON EUTECTIC FIXED POINT FOR THERMOCOUPLE CALIBRATION

*Suherlan*<sup>1,2,3</sup>, and *Yong-Gyoo Kim*<sup>1</sup>

<sup>1</sup> KRISS, 267 Gajeong-Ro, Yuseong-Gu, Daejeon 305-340, Republic of Korea

<sup>2</sup> UST, 217 Gajeong-Ro, Yuseong-Gu, Daejeon 305-350, Republic of Korea

<sup>3</sup> KIM-LIPI, Kompleks PUSPIPTK Gedung 420, Tangerang Selatan, Banten, Indonesia  
[dragon@kriss.re.kr](mailto:dragon@kriss.re.kr)

**Abstract:** Three Si-SiC eutectic fixed-point cells have been constructed using electrically heated furnace for use in thermocouple thermometry. The first two cells were made from silicon powder mixed with carbon while the third was made from pure silicon. The first cell with a conventional graphite crucible was early broken during the preliminary test, so the result could not be recorded. The second cell with a modified graphite crucible, thicker and shorter than the previous one, was able to withstand until 36 melt-freeze cycles and was held above 1400 °C for about 143 h, but unfortunately this cell was also finally broken after the test. The third cell, made from pure silicon filled in the modified crucible, was successfully tested without any mechanical failure. This cell was held above 1400 °C for approximately 157 h and was subjected to 36 melt-freeze cycles, where 7 cycles of them was realized from room temperature. The melting plateau of the cell lasted about 40 min and the extreme of the measured inflection point differed by 0.1 °C. The repeatability, represented by its standard deviation, was 0.03 °C. The temperature difference between both of the last two cells was calculated to be 0.5 °C.

**Keywords:** Eutectic fixed-points, Si-C, Thermocouple

### 1. INTRODUCTION

Si-SiC was suggested as a potential high temperature eutectic fixed-point as early as 2010 by S. Y. Kwon et al. and they reported that the melting temperature of Si-SiC measured by differential scanning calorimetry (DSC) was  $(1406.7 \pm 0.1)$  °C [1]. Si-C system is of interest especially for use as a fixed-point for thermocouple calibration above the freezing points of Ag, Au, and Cu because its melting temperature is near the upper limit of the useable range of Pt/Pd thermocouples. Furthermore silicon in a very high purity can be easily obtained from the market with relatively lower price especially compare than palladium. Table 1 shows the possibility of using Si-C system as an alternative new fixed-point to replace the expensive Pd-C eutectic fixed-point.

To establish a metal-carbon fixed-point, first of all is to identify the eutectic point using phase diagrams. After that, a eutectic fixed-point should be made and its reproducibility and other thermal behavior need to be investigated. In this

work we used pure silicon and carbon powder as the fixed-point material and filled them in graphite crucible. The Si-SiC eutectic point has melting and freezing temperatures lower than the pure silicon (~1414 °C) [3], but as long as the plateau is reproducible, this eutectic melting and freezing temperatures can be used as references point [4].

The other important thing to be considered is the coefficient of thermal expansion (CTE) of the crucible as well as the eutectic materials. It was found that the CTE varied significantly between different graphite grades. The ingot forms at high temperature so, if the CTE of the crucible is greater than that of the ingot, it will break when cooled as the crucible shrinks more than the ingot, i.e. robust fixed-points require that the thermal expansion of the graphite be lower than that of the eutectic. This is particularly a problem for the eutectics that have the lowest coefficients of thermal expansion [5].

In this article, we report only the measurement results of the last two cells (Si-SiC 2 and Si-SiC 3) while the first cell (Si-SiC 1) was not recorded due to the early broken during the preliminary test, but its causes will be shortly discussed. The Si-SiC 1 and Si-SiC 2 were made from silicon powder mixed with 0.7% of C which filled into the graphite crucible type I (conventional type) and type II (thicker and shorter than type I) respectively, while the Si-SiC 3 was made from pure silicon powder filled in the crucible type II. The repeatabilities as well as the temperature differences of the cells were investigated using type S thermocouple, and then the result will be mainly discussed.

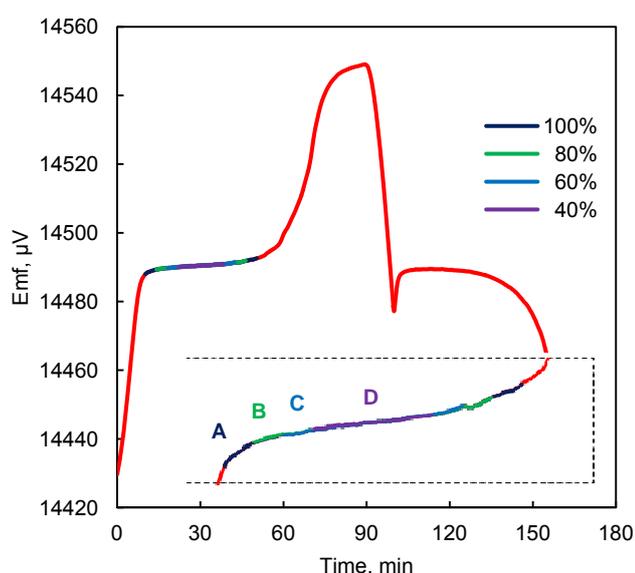
**Table 1** The possibility to use the Si-C system among the known eutectic fixed points [4] to replace the expensive Pd-C

| Metal-Carbon Eutectic | Approximate Temperature/ °C |
|-----------------------|-----------------------------|
| Fe-C                  | 1153                        |
| Co-C                  | 1324                        |
| Ni-C                  | 1329                        |
| <b>Pd-C ← Si-C</b>    | <b>1492 ← 1406</b>          |
| Rh-C                  | 1657                        |
| Pt-C                  | 1735                        |
| Ru-C                  | 1954                        |
| Ir-C                  | 2291                        |
| Re-C                  | 2474                        |

## 2. EXPERIMENTAL METHOD

A vertical, single-zone furnace using molybdenum disilicide (MoSi<sub>2</sub>) heating elements was used as both the casting and measuring furnace for the study of Si-SiC eutectic fixed-point applied to thermocouple calibration. The recommended highest achievable temperature of this furnace is about 1600 °C, even though the heating elements can be used up to 1800 °C. A type S thermocouple assembled in-house was used to monitor the melting-freezing plateau of the cells. The reference junction, encased with stainless steel sheath, was a normal ice-water mixture. This thermocouple was connected to a digital voltmeter by pure copper wires. The thermal emf of the thermocouple was measured using nanovoltmeter, model 2128A made by Keithley Instruments. A computer-based data acquisition system was used to collect data for 3 s time intervals. Figure 1 shows the typical melting and freezing curve of the Si-SiC eutectic fixed-point measured by type S thermocouple.

The crucibles used for the Si-SiC eutectic cells were made of pure graphite. This graphite material has a nominal purity of 99.999%. The crucible type I, used for Si-SiC 1, has an inner and outer diameter of 24 mm and 36 mm respectively, while the crucible type II, used for Si-SiC 2 and Si-SiC 3, was 32 mm and 46 mm respectively. The inner length for both the type I and II were 112 mm and 71 mm respectively. By a simple calculation we concluded that the crucible type II was thicker and shorter than type I. A small-hole with 1 mm of diameter on the top side of thermocouple well was designed as ventilation to overpass all things due to the thermal expansion of the material during the heating process. Figure 2 shows the schematic and photograph of the graphite crucible type II used for Si-SiC 2 and Si-SiC 3.



**Figure 1** Typical melting and freezing curve of the Si-SiC eutectic fixed-point measured by type S thermocouple. (A), (B), (C), and (D) were the 100%, 80%, 60% and 40% of the estimated melting curves respectively. The melting point was determined by averaging the inflection point of the melting curves B, C and D.

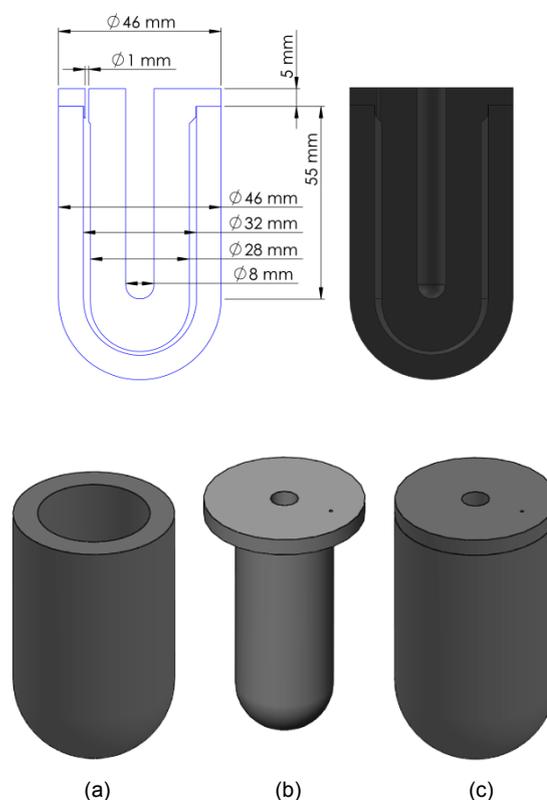
**Table 2** The materials and crucibles used in making Si-SiC eutectic fixed-points

| Cell ID     | Si-SiC 1 | Si-SiC 2 | Si-SiC 3 |
|-------------|----------|----------|----------|
| Mass (gram) | 54.67    | 24.79    | 24.70    |
| Material    | Si + C   | Si + C   | Si       |
| Crucible    | Type I   | Type II  | Type II  |

The volumes of the space between the thermocouple well and the crucible, which was filled with the eutectic materials, were calculated to be 26.1 cm<sup>3</sup> of the type I and 11.8 cm<sup>3</sup> of the type II.

The pure silicon of 99.999% and carbon of 99.9995% powder used in this work were obtained from Alfa Aesar with the mesh size of -100+325 and -325 respectively. About 90% of the available space in the crucible was filled with these eutectic materials. The Si-SiC 1 and Si-SiC 2 cells were respectively made from 54.67 gram and 24.79 gram of silicon powder mixed with 0.7% of carbon, while the Si-SiC 3 cell was made from 24.70 gram of pure silicon powder. Table 2 shows the specific amounts of the eutectic materials and the crucibles used in making Si-SiC eutectic fixed-points.

To investigate the Si-SiC 2 cell, the temperature of the furnace was initially set to 10 °C below the expected transition temperature that was determined from preliminary experiments, and temperature was maintained at this value for a period of 30 min. The furnace temperature was then raised 6 °C above the transition temperature with a rate of 1 °C min<sup>-1</sup>, and the temperature was then also maintained at this value for a period of 30 min.



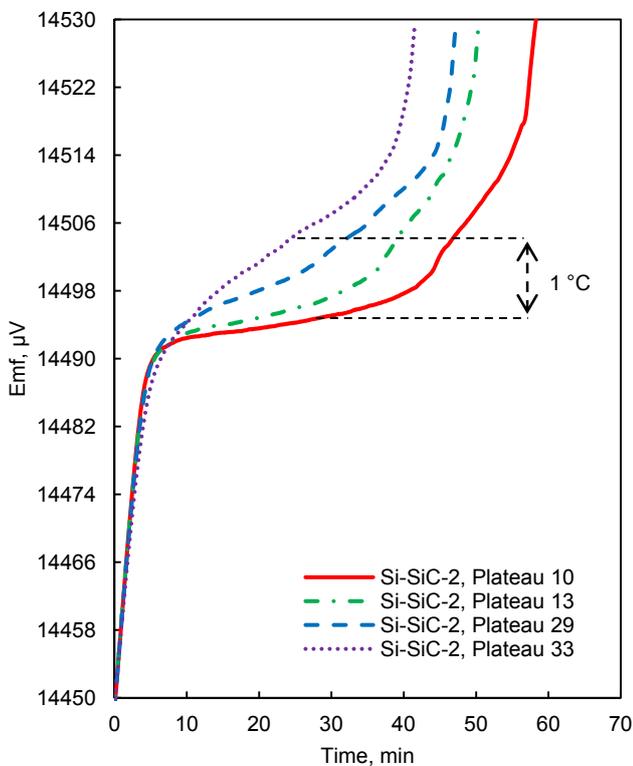
**Figure 2** Schematic (up) and photograph (down) of the graphite crucible type II. (a), (b), and (c) are the crucible, the thermocouple well, and the assembled crucible

The set temperature was once again lowered to a temperature of 10 °C below transition temperature to conclude one full measurement cycle. Thirty six melt-freeze cycles measurements were performed to evaluate the repeatability of the Si-SiC 2cell. In the case of Si-SiC 3 cell, the temperature of the furnace was set to 5 °C higher and 5 °C lower than the expected transition temperature, then thirty six melt-freeze cycles were also performed to evaluate the repeatability of this cell. In each process of the Si-SiC cell fabrication, as well as during the measurements on the transition point, the atmosphere inside the cell was maintained as argon gas with a volume fraction of 0.5% hydrogen, whose pressure was controlled to slightly above ambient.

### 3. RESULTS

Fixed-point Si-SiC 1 (made from silicon mixed with carbon in the crucible type I) was early broken during the preliminary test. We supposed the crucible type I used for this cell was not strong enough for making Si-SiC cell, so we modified the crucible to be thicker and shorter, and of course would be more robust than the previous one.

Fixed-point Si-SiC 2, used the same material with the Si-SiC 1, was held above 1400 °C for approximately 143 h and was subjected to at least 36 melt-freeze cycles (4 cycles from room temperature to the melting temperature). The first 10 cycles was a preliminary test to find the expected transition point, and then the last 26 cycles was to find the repeatability of the melting point.



**Figure 3** Selected melting plateaus of the Si-SiC 2 fixed-point. The plateaus were chosen to represent the extremes of the measured inflection points differed by 1 °C

The average emf measured by type S thermocouple was 14497 μV with the standard deviation of 3.8 μV. The maximal variations among the melting plateaus was observed between the 10<sup>th</sup> and the 33<sup>rd</sup> plateaus differed by 1 °C. Figure 3 shows four selected melting plateaus represented the maximal variation in the inflection points of Si-SiC 2 measurements.

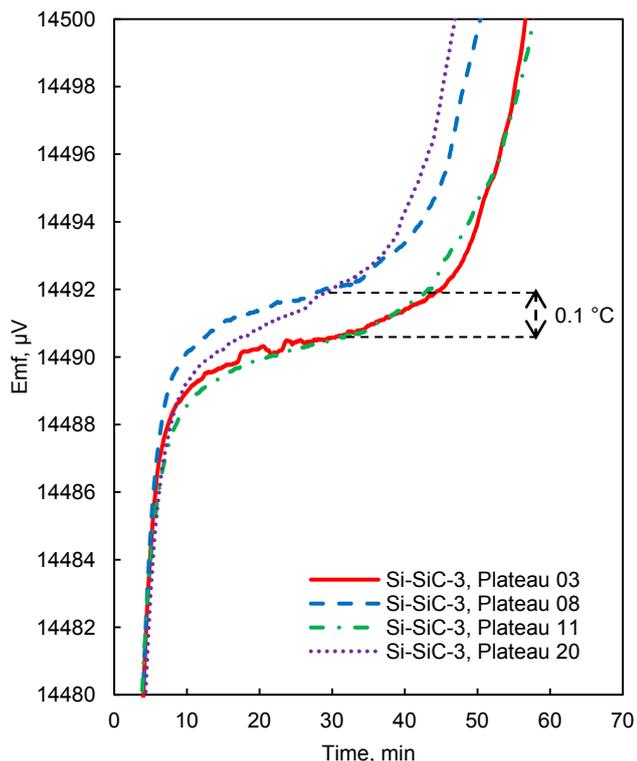
After performing the 36 melt-freeze cycles measurement, unfortunately, the cell was then broken. The outer crucible showed a crack after the temperature of the furnace was cooled down to room temperature at last cycle of the test. No materials flowed out from the crucible, this means that the crucible was cracking during the freezing state of the cell. We provisionally supposed that this occurred due to the CTE of the crucible could be greater than the eutectic materials. The CTE of silicon was reported as 2.616~4.612 ( $10^{-6} \text{ K}^{-1}$ ) in the range of 300~1600 K [5]. During the experiments, particularly when the temperature of furnace was cooling down to room temperature, these values could be possibly lower than the CTE of commercial graphite of 1.2~8.2 ( $10^{-6} \text{ K}^{-1}$ ) [6]. If this happened then the cell would be broken as the crucible shrank more than the eutectic materials.

After performing the repeatability test (36 melt-freeze cycles), a large amount of silicon vapor was found attached to the crucible especially on the top of the cell around the ventilation hole. Some of alumina discs (used to keep the radiation heat) near the cell were also found to become grayish and brittle due to the reaction with silicon vapor. Figure 4 shows the Si-SiC cell and the brittle alumina discs after performing the test of 36 melt-freeze cycles.

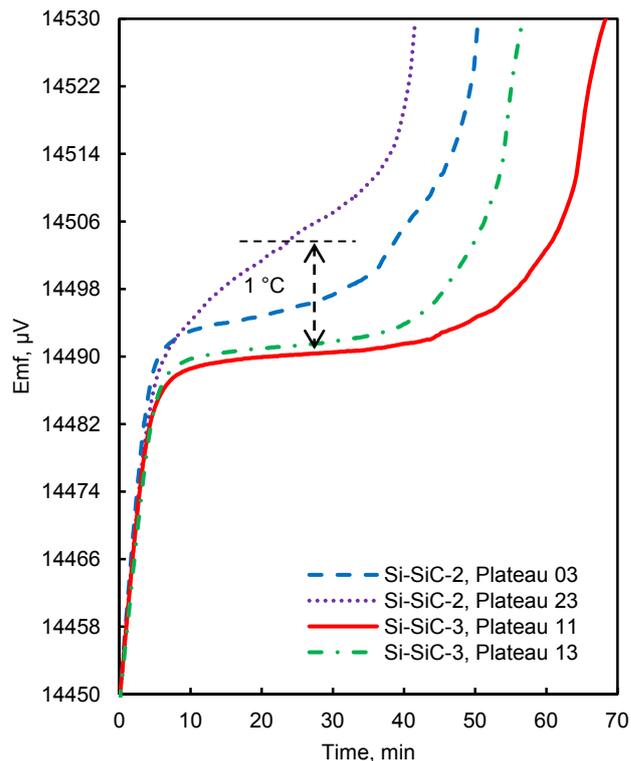
In the case of Si-SiC 3 cell (made from pure silicon powder filled in the crucible type II), the fixed-point was held above 1400 °C for approximately 157 h and was subjected to at least 36 melt-freeze cycles where 7 cycles of them was realized from room temperature to the melting temperature. The average emf measured by the same thermocouple was 14491 μV with the standard deviation of 0.4 μV. The maximal variation in the inflection points was extremely differed by 0.1 °C. It was ten times better than the Si-SiC 2.



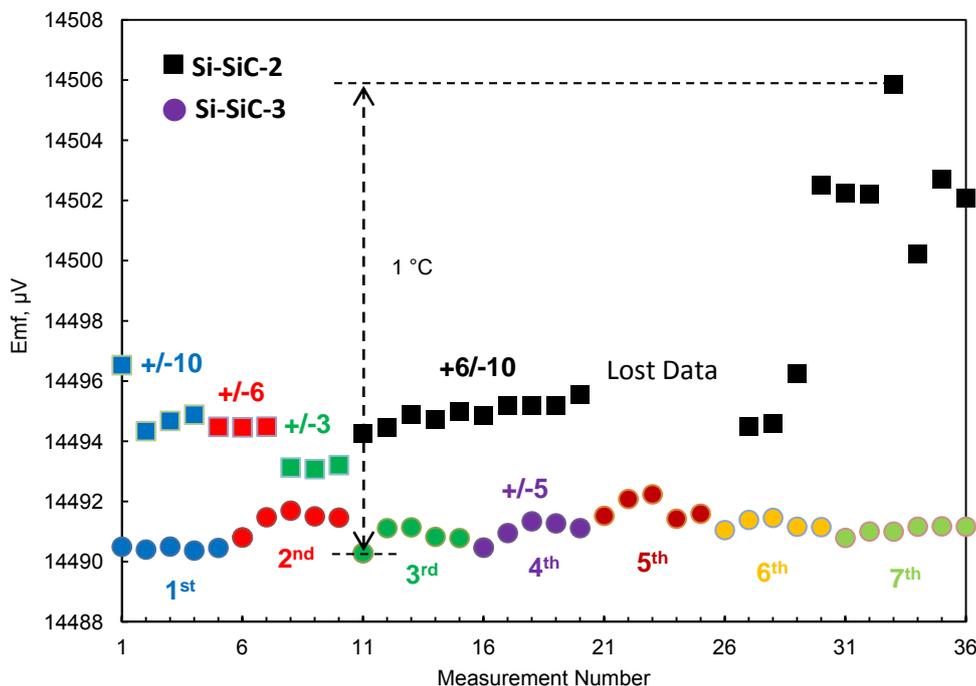
**Figure 4** Silicon vapour was found attached to the crucible around the ventilation hole (*left*) and the alumina discs become brittle after reaction with silicon vapour (*right*)



**Figure 5** Selected melting plateaus of the Si-SiC 3 fixed-point. The plateaus were chosen to represent the extremes of the measured inflection points differed by 0.1 °C



**Figure 6** Selected melting plateaus of the Si-SiC 2 and Si-SiC 3 fixed-points. The plateaus were chosen to represent the extremes of the measured inflection points differed by 1 °C



**Figure 7** Melting points for all measurements of Si-SiC 2 and Si-SiC 3 measured by type S thermocouple. Variations in temperature setting of Si-SiC 2 (indicated by blue, red, green and black squares) were +/- 10 °C, +/- 6 °C, +/- 3 °C and +6/-10 °C respectively, but unfortunately some data (of +6/-10 °C) were missing due to the error on the data acquisition software when recording the 11<sup>th</sup> to 16<sup>th</sup> plateaus. The coloured circles indicate the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> set of measurements of Si-SiC 3 where each set has five melt-freeze cycles. The extreme inflection points on both of the cells were about 1 °C

Figure 5 shows four selected melting plateaus represented the maximal variation in the inflection points of Si-SiC 3 measurements. This cell was successfully tested with no mechanical failure on the crucible as well as the thermocouple well.

The melting plateaus of the Si-SiC 2 and the Si-SiC 3 cells lasted about 30 min and 40 min respectively. Figure 6 shows selected melting plateaus for both Si-SiC 2 and Si-SiC 3 measured by type S thermocouple. These four plateaus represent the maximal variation in the inflection

points observed during the measurements. The plateaus with the highest (plateau 23 of Si-SiC 2) and lowest (plateau 11 of Si-SiC 3) inflection points differed by 1 °C. The melting point was determined by averaging the inflection point of 80%, 60%, and 40% of the complete melt. The inflection point of all melting curves was determined from the minimum of derivative of the cubic polynomial fitted to the plateaus.

Figure 7 also shows the melting points, indicated by the inflection points for each melting plateaus, for all measurements of the Si-SiC 2 and the Si-SiC 3 fixed-points, but unfortunately some of the Si-SiC 2 data were missing due to the error on the data acquisition software when recording the 11<sup>th</sup> to 16<sup>th</sup> plateaus.

The Si-SiC 3 was measured in seven stages which each stage was started from room temperature to the melting state. The first stage, indicated by the blue circle, was the first 5 cycles, and then followed by the second, the third and so on until the seventh 5 cycles were indicated by the red, the green and so on until the light green circles respectively. In the thirty six measurements on the Si-SiC 2 cell, the repeatability of the transition temperature, represented by the standard deviation, was 0.3 °C, and in the case of Si-SiC 3 cell the repeatability was ten times better than the Si-SiC 2 by 0.03 °C.

#### 4. CONCLUSION

Three Si-SiC eutectic fixed-points have been produced and the melting behaviours of the last two cells have also investigated. The first cell (Si-SiC 1) was early broken during the preliminary test. We supposed the crucible (type I), used for this cell, was not strong enough to withstand the eutectic material inside the cell during the melting-freezing process. The second cell (Si-SiC 2) was made from 24.79 gram silicon and carbon filled in the crucible type II (thicker and shorter than type I). This cell was held above 1400 °C for approximately 143 h, but unfortunately this cell was also finally broken after 36 melt-freeze cycles of the test. The

third cell (Si-SiC 3) was made from 24.70 gram pure silicon powder filled in the crucible type II. This last cell was successfully tested without any mechanical failure. This cell was held above 1400 °C for approximately 157 h and was subjected to 36 melt-freeze cycles, where 7 cycles of them was realized from room temperature. The melting plateau of the cell lasted about 40 min and the extreme of the measured inflection point differed by 0.1 °C. The repeatability, represented by its standard deviation, was 0.03 °C. The temperature difference between both of the last two cells was calculated to be 0.5 °C. Further studies and experiments are necessary to evaluate the reproducibility as well as the reliability of the Si-C system.

#### 5. REFERENCES

- [1] S. Y. Kwon, Y. -G. Kim, and I. Yang, "Study on the melting and freezing behaviour of high temperature binary fixed points using differential scanning calorimetry", *Metrologia*, vol. 47, no. 3, pp. 248-252, April 2010.
- [2] K. C. Mills, *Recommended values of thermophysical properties for selected commercial alloys*. Woodhead Publishing Limited, pp. 191, 2002.
- [3] Y. Yamada, H. Sakate, F. Sakuma, and A. Ono, "Radiometric observation of melting and freezing plateaus for a series of metal-carbon eutectic points in the range 1330 °C to 1950 °C", *Metrologia*, vol. 36, no. 3, pp. 207-209, June 1999.
- [4] E. R. Woolliams, G. Machin, D. H. Lowe, and R. Winkler, "Metal (carbide)-carbon eutectics for thermometry and radiometry: a review of the first seven years", *Metrologia*, vol. 43, no. 6, pp. R11-R25, November 2006.
- [5] Virginia Semiconductor Inc., "Basic Mechanical and Thermal Properties of Silicon", pp. 2.
- [6] Azom.com, "Classification, Properties, and Application of Graphite", URL accessed on February 15, 2012.
- [7] I. Yang and Y. -G. Kim, "Short Communication: The potential for using the hypereutectoid transition in Fe-C in thermocouple thermometry", *Metrologia*, vol. 44, no. 2, pp. L10-L13, March 2007.