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MELTING TEMPERATURE OF SI-SIC EUTECIC FIXED POINT

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Abstract – The temperature of the Si–SiC eutectic fixed point for use in thermocouple thermometry has been determined. Three Si–SiC cells were fabricated and melting transition was measured using three types of thermocouple: one type S, one type B, and two Pt/Pd thermocouples calibrated at the fixed points of Ag, Cu, Fe–C, Co–C, and Pd (only for type B). The transition temperature, measured using the type S and two Pt/Pd thermocouples, was 1410.0 ± 0.8 °C with $k = 2$.

Keywords: Thermocouple, Si-SiC, eutectic point, melting temperature

1. INTRODUCTION

The Si–SiC eutectic fixed point has been studied at KRISS as a new alternative fixed point for use in thermocouple thermometry, in addition to the well-known metal–carbon eutectic fixed points. The Si–SiC eutectic is of interest because its melting temperature is near the upper limit of the usable range of Pt/Pd thermocouples. Furthermore, high purity silicon can be obtained easily and cheaply, especially when compared with palladium. Therefore, there is the potential to use the Si–SiC eutectic fixed point instead of the more expensive Pd–C eutectic fixed point [1]. In this paper, we report on the determination of the transition temperature of the Si–SiC eutectic fixed point. Each of the three Si–SiC cells used was made from pure silicon powder within a graphite crucible. After fabrication, a type S thermocouple (designated as KSTC) was used to measure the first five plateaus of each cell as a preliminary test to investigate their melting–freezing plateau behaviour. Four other thermocouples (another type S designated as HSTC, one type B designated as HBTC, and two Pt/Pd thermocouples designated as HPtPd_1 and HPtPd_2), calibrated at several fixed points (Ag, Cu, Fe–C, Co–C, and an additional Pd fixed point for the type B thermocouple) were used to measure the transition points of the melting plateaus. A weighted mean was calculated as the combined result of 30 melting plateau transitions measured using the four thermocouples. The associated uncertainty of the temperature determination was also evaluated.

2. EXPERIMENTAL DETAILS

Figure 1 shows a schematic drawing and a cross-sectional view of the graphite crucible used for the Si–SiC cells. The length of the assembled crucible was 83 mm and the depth of the thermometer well was 60 mm. The outer diameter of the crucible was 46 mm, and the inner diameter of the thermometer well was 8 mm. The thicknesses of the crucible and the thermometer well were 7 mm and 10 mm, respectively. The volume of the space between the thermocouple well and the crucible, which would be filled with silicon powder, was calculated to be 11.8 cm^3.

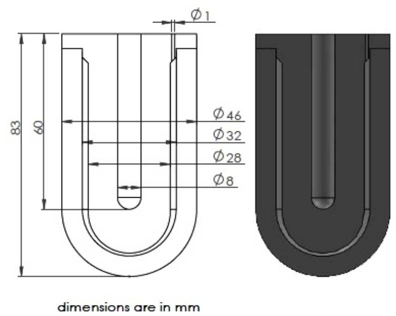

Fig. 1. Schematic drawing and cross-sectional view of the graphite crucible used for the Si–SiC cells.

Three set of Si–SiC cells were made using a charge of 24.78, 24.72, and 24.71 g of pure silicon powder, respectively. Four calibrated thermocouples (HSTC, HBTC, HPtPd_1 and HPtPd_2) used in our experiments were assembled and tested in-house. A vertical single-zone furnace with molybdenum disilicide ($MoSi_2$) heating elements was used for both fabricating and measurements using the Si–SiC eutectic fixed point cells. The furnace was uniform within ± 1.0 °C up to a distance of 10 cm from the bottom of the furnace. Because the length of the Si–SiC cell was 8.3 cm, it was thought that this furnace would be adequate for realizing the Si–SiC eutectic fixed points. The temperature of the furnace was initially set at 5 °C below the expected transition temperature (approx. 1405 °C) determined from preliminary experiments, and the temperature was maintained at this value for a period of 1 h. The furnace temperature was then increased to 5 °C above the transition temperature (approx. 1415 °C) at a rate of 1 °C min^{-1} and maintained at this value for a further period of 2 h.

3. RESULTS AND DISCUSSIONSUBMISSION

Figure 2(a) shows the melting plateaus of three Si–SiC cells measured using the two Pt/Pd thermocouples (HPtPd_1 and HPtPd_2). Initially HPtPd_1 was assigned to measure the sixth to the eighth plateau of each cell. However, this thermocouple broke at the measuring junction when it was employed to measure the second cell, and it broke again at the palladium wire near the measuring junction when used for the third cell. As a consequence, the sixth to the eighth melting plateaus of the last two cells (Cell_2 and Cell_3) were not recorded. HPtPd_2 was employed to measure the last three plateaus (the fifteenth to the seventeenth cycle) of each cell. The transition points of the melting plateaus measured by HPtPd_1 (the sixth to the eighth cycle) and the final melting plateaus measured by HPtPd_2 (the fifteenth to the seventeenth cycle) were repeatable to within 0.3 °C, and the extremes of the measurements differed by 0.8 °C. To determine the melting temperature, the calibration equation of both Pt/Pd thermocouples was extrapolated out of their calibration range (the upper limit of approx. 1324 °C) to a temperature of approx. 1410 °C, which is close to the melting transition temperature of the Si–SiC eutectic point.

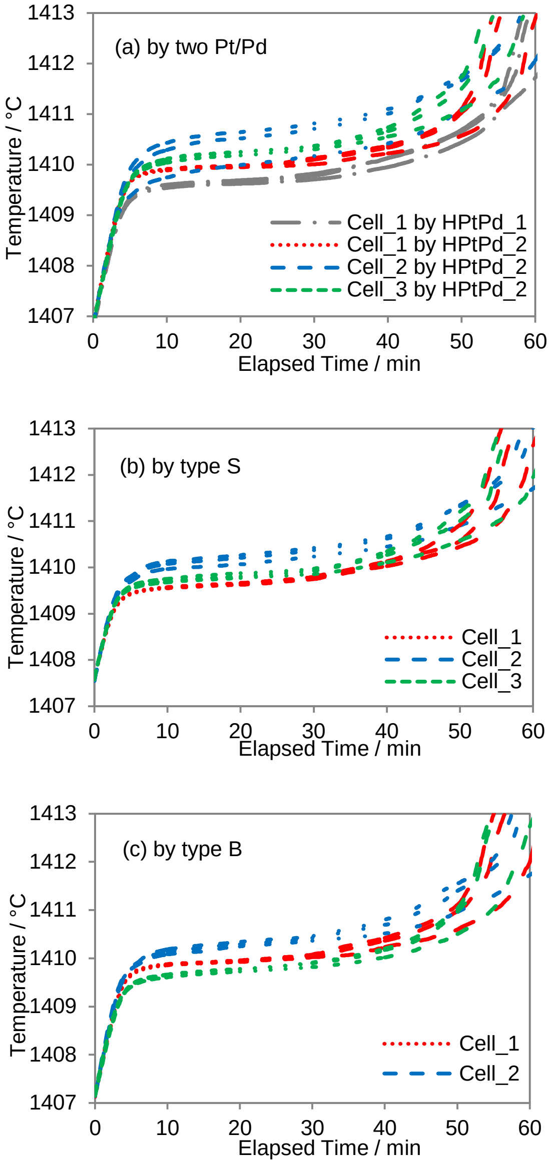

Fig. 2. Melting transitions of the three Si–SiC cells measured using: (a) two Pt/Pd, (b) a type S, and (c) a type B thermocouple. The transition temperature was determined to be 1410.1 °C for the Pt/Pd thermocouples, 1409.9 °C for the type S thermocouple, and 1410.0 °C for the type B thermocouple.

A transition temperature of 1410.1 °C was obtained using this method. It was confirmed that either a linear or a quadratic extrapolation adequately fitted both Pt/Pd thermocouples. The absolute extrapolation errors were evaluated by measuring the EMF of the thermocouples at 1400 °C in a block comparison system measured using a standard radiation thermometer [2]. The errors were calculated to be 0.08 °C for HPtPd_1 and 0.03 °C for HPtPd_2. These values are considered valid up to 1410 °C.

Figure 3(b) shows the melting plateaus (the ninth to the eleventh cycle) of the three Si–SiC cells measured using the type S thermocouple (HSTC). The transition point of the melting plateaus was repeatable to within 0.2 °C, and the extremes of the measurements differed by 0.6 °C, which was slightly better than the result obtained using the Pt/Pd thermocouples. In a similar manner to HPtPd_1 and HPtPd_2, thermocouple HSTC was also extrapolated linearly up to 1410 °C. The uncertainty was evaluated at 1400 °C by comparing the EMF of the thermocouple against a standard radiation thermometer. The temperature difference between the extrapolated value and the reference value was 0.07 °C. A transition temperature of 1409.9 °C was obtained using this method.

Figure 3(c) shows the melting plateaus (the twelfth to the fourteenth) of the three Si–SiC cells measured using the type B thermocouple (HBTC). Similar to the results of the HSTC thermocouple, the transition point of the melting plateaus of the Si–SiC cells measured using HBTC was repeatable to within 0.2 °C, and the extremes of the measurements differed by 0.6 °C. Unlike the previous three thermocouples (HPtPd_1, HPtPd_2, and HSTC), HBTC was calibrated up to the Pd fixed point (1554.8 °C) [10]; therefore, a usual interpolation was adequate to determine the transition temperature around 1410 °C. However, owing to the large temperature difference between the two highest calibration points (Co–C and Pd points), an additional measurement was required. In a similar manner to the previous thermocouples, HBTC was measured at a temperature of 1450 °C in a block comparison system using a standard radiation thermometer to evaluate the interpolation error. The error was calculated to be 0.2 °C. We believe that this value is also appropriate for the temperature of 1410 °C. A transition temperature of 1410.0 °C was obtained using this method.

Table 1 shows a summary of the temperature measurement data of the three Si–SiC cells measured using the four calibrated thermocouples. The combined result was determined by calculating the weighted mean of the 30 melting plateau transitions. The weighted mean, denoted by x_{W}, was defined as $x_{\mathrm{W}} = \sum_i w_i x_i / \sum_i w_i$, with weights $w_i = 1/u^2(x_i)$ for i = 1, …, n and u being the standard uncertainty.

Table 1. Type size for manuscript (in points).

Thermocouple used	Temperature (°C)		
	Cell_1	Cell_2	Cell_3
HPtPd_1	1409.8 ± 0.8	–*	–*
HSTC	1409.7 ± 0.8	1410.3 ± 0.8	1409.8 ± 0.8
HBTC	1410.0 ± 1.5	1410.3 ± 1.5	1409.8 ± 1.5
HPtPd_2	1409.9 ± 0.8	1410.4 ± 0.8	1410.2 ± 0.8

Figure 3 shows a summary in graph form of the temperature measurements based on the data in Table 1. Based on these results, we concluded that the extremes in the melting temperature of these three Si–SiC cells differed by 0.8 °C. The repeatability of the three Si–SiC cells was calculated to be 0.3 °C. The associated uncertainty (k = 2) is represented by the error bars in Figure 3. The lower limit (LL) temperature of 1408.3 °C and the upper limit (UL) temperature of 1411.8 °C were obtained by adding the uncertainty values into the data. Based on this calculation, we expected that the measurement data would be within the range of LL and UL.

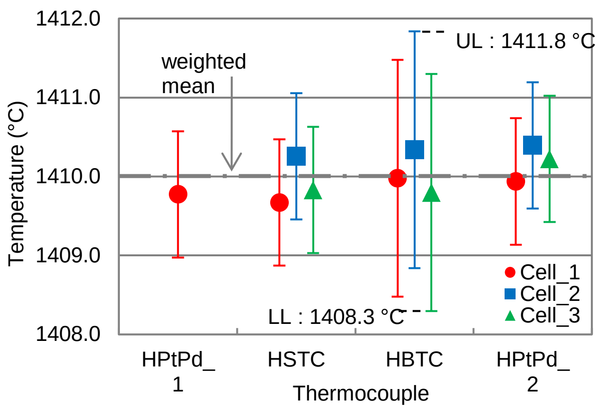

Fig. 3. Summary of the melting temperatures of three Si–SiC cells measured using four thermocouples. The lower limit (LL) and the upper limit (UL) were calculated to be 1408.3 °C and 1411.8 °C, respectively.

4. UNCERTAINTY CALCULATION

The uncertainty of the temperature measurements of the three Si–SiC cells using three types of thermocouples was evaluated. The uncertainty in the thermocouple calibration (u_{cal}) at the freezing points of Ag, Cu, Fe–C, Co–C, and Pd (only for type B) was assumed to be that described previously [2].

The uncertainty in the extrapolation of the calibration equation (u_{ext}) was estimated from the difference between the extrapolated value and the reference value measured using a standard radiation thermometer. The uncertainty was calculated to be 0.042 °C for HSTC and 0.034 °C for both HPtPd_1 and HPtPd_2 thermocouples. A third-order polynomial equation was used to interpolate the data of the type B thermocouple. The uncertainty was taken to be the standard error of the deviated data (the deviation of the interpolated data against the measured data). The uncertainty was calculated to be 0.125 °C at 1410 °C. Both the extrapolated and interpolated results were evaluated by comparing the EMF of the thermocouples against a standard radiation thermometer in a block comparison system.

The temperature of the reference ice point junction was stable to within ± 0.01 °C during the measurements, and the standard uncertainty (u_{ref_j}) was estimated to be 6 mK. The change in EMF (drift) was studied at the freezing point of silver before, and after the measurements to assess the short-term stability of the thermocouple. The uncertainty because of this factor (u_{sta}) at the Ag freezing point was estimated to be 0.001 °C for HSTC, 0.019 °C for HBTC, 0.052 °C for HPtPd_1, and 0.089 °C for HPtPd_2. The digital voltmeter (DVM) used was calibrated at KRISS, and its relative expanded uncertainty was determined to be 8 × 10^{-6} (k = 2). The short-term stability value of the DVM was assumed to be the same as that described in the equipment operational manual. The standard uncertainty of the DVM (u_{DVM}) from both components was estimated to be 6–10 mK.

The uncertainty in the NIST/IMGC reference function (u_{ref_f}) for the Pt/Pd thermocouple was estimated to be 4.5 μV (which corresponds to 0.179 °C at 1410 °C) as reported [3]. The error in temperature calculated using an IEC inverse function (for the type S and type B thermocouples), relative to the reference function, was < 0.06 °C [4]. The uncertainty from this component (u_{ref_f}) was estimated to be 0.035 °C. The uncertainty in determining the transition point of the melting plateau (u_{trans}) was estimated from the difference between the two datasets obtained using two different methods. The repeatability (u_{rep}) was taken as the standard deviation of the transition points of the three Si–SiC cells (Cell_1 to Cell_3) measured using each thermocouple. The combined standard uncertainty (u_c) was calculated by adding in quadrature of the entire components. Table 2 shows the sources and estimated values for each component that contributed to the uncertainty of the melting temperature of the Si–SiC cells measured using three types of thermocouple.

Table 2. Sources and estimates of the uncertainty of the components.

Uncertainty component	Standard uncertainty		
	Pt/Pd	Type S	Type B
Calibration at fixed points, u_{cal}	0.330	0.340	0.387
Thermocouple inhomogeneity, u_{inh}	0.104	0.154	0.649
Extrapolation of calibration, u_{ext}	0.034	0.042	–
Interpolation, u_{int}	–	–	0.125
Ice point realization, u_{ref_j}	0.006	0.006	0.006
Short-term instability of thermocouple, u_{sta}	0.089	0.001	0.019
DVM instability and uncertainty, u_{DVM}	0.007	0.010	0.006
Thermocouple reference function, u_{ref_f}	0.179	0.035	0.035
Determination of the transition point, u_{trans}	0.013	0.028	0.006
Repeatability of the inflection point, u_{rep}	0.083	0.088	0.080
Combined standard uncertainty, u_c	0.407	0.390	0.771
Expanded uncertainty (k = 2), U	0.8	0.8	1.5

5. CONCLUSIONS

By applying the method previously discussed [5], three Si–SiC cells were constructed and each was operated through 17 melt–freeze cycles without observing any sign of mechanical failure. However, without proper handling, the cells can be easily broken. The raw materials (silicon powder) used were relatively cheap, especially when compared with palladium. It required a small volume of silicon (approx. 25 g in each cell) to construct the Si–SiC cells. The transition temperature of the Si–SiC eutectic, measured using the type S and two Pt/Pd thermocouples, was determined to be 1410.0 ±

0.8 °C (k = 2). The four thermocouples used in this experiment were calibrated at several fixed points, and the scale was further validated using a standard radiation thermometer [2]. However, the calibration uncertainty of the type B thermocouple was much larger than that of the other thermocouples. We supposed that this was due to the result of an overestimated inhomogeneity of the type B thermocouple that was performed at a low temperature of 180 °C. In another experiment, a well-prepared Si–SiC cell was repeatable to within 0.03 °C, and was successfully tested through 80 melt–freeze cycles without experiencing any breakages [5]. In the present study, the three Si–SiC cells used were repeatable to within 0.3 °C, and were still in working condition after 17 melt–freeze test cycles. Based on these results, we conclude that there is the potential for using the Si–SiC eutectic as a new eutectic fixed point, in addition to the well-known eutectic fixed points.

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