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Realization of Fe–C Eutectic Point Using an Alumina Crucible

Y.-G. Kim · K. S. Gam · I. Yang

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Abstract As another crucible material for metal–carbon eutectic points, alumina ceramic was used in the first trial to make an Fe–C eutectic point for the calibration of a thermocouple. Its melting and freezing behavior was tested 26 times with a type S thermocouple at various melting offset temperatures, namely, +4 °C, +9 °C, and +19 °C, and at a fixed freezing offset temperature of −11 °C. The melting emf is reproducible independent of the melting offset temperatures, and the standard deviation of the 26 melting temperatures is 0.02 °C without breakage of the cell. The difference of melting emf between alumina Fe–C and graphite Fe–C fixed points is only 25 mK within an uncertainty of 0.39 °C ($k = 2$). The melting behaviors of an alumina cell are quite similar to a common graphite cell. Thus, alumina can be used as a crucible material in an Fe–C eutectic system without breakage, and it can be used at a higher temperature range. As possible application systems using alumina crucibles, Pd–C and Si–SiC eutectic points are suggested.

Keywords Alumina crucible · Fe–C eutectic point · Melting temperature · Reproducibility · Thermocouple

1 Introduction

Metal–carbon (M–C) eutectic points are very promising as secondary fixed points at temperatures higher than the Cu freezing point. The melting temperatures of some selected M–C eutectic points are expected to be assigned by CCT WG2 (Working Group) in cooperation with WG5. These points can be used to calibrate thermometers

Y.-G. Kim (✉) · K. S. Gam · I. Yang
Center for Temperature and Light, Division of Physical Metrology, Korea Research Institute of Standards and Science, Yuseong, Daejeon 305-340, Korea
e-mail: dragon@kriss.re.kr

or to check the linearity of a radiation thermometer. Particularly Fe–C, Co–C, Pd–C, and Pt–C eutectic points have been widely investigated for the calibration of thermocouples [1–6]. In addition, international comparisons of the M–C points by using thermocouples as transfer artifacts are in progress at EUROMET and the APMP [7].[1]

For these important M–C cells, graphite is always used as a crucible material because it is one of the constituent elements of eutectic alloys and is inert chemically. In spite of the absence of reporting on the compositional change by successive melting and freezing reactions in the M–C system, the feasibility of the composition inside the alloy being changed to a hypereutectic composition is considered reasonable due to the excess of carbon from the crucible. Thus, the melting behavior may possibly change after long-term exposure to high temperature. Another crucible material (other than graphite) with mechanical and chemical inertness may prevent any compositional change.

In this work, alumina is used instead of graphite as another crucible material. An alumina crucible is chemically immune to reaction with graphite and many metals, even though it is somewhat more difficult to machine than common graphite. Previously alumina crucibles were used to construct pure metal high-temperature fixed points such as Ni and Pd [8,9]. In our first approach to using the new crucible, we selected the Fe–C system, which is known to have the lowest melting temperature of all the M–C systems. We also investigated its melting and freezing behaviors at various melting offset temperatures. Our goal in this work is to evaluate the possibility of using a ceramic material as a crucible material for a high-temperature fixed point.

2 Experimental Details

A double-wall alumina crucible and a thermometer well were prepared as shown in Fig. 1. Alumina crucibles were made using pure alumina powder having a purity of 99.8 %. The cell was 100 mm long and 33 mm in diameter. The wall thicknesses of the inner and outer crucible are 3.5 mm and 4 mm, respectively. The thermometer well had an external diameter of 14 mm and an internal diameter of 6 mm. The volume of the cell was about 8.25 cm^3. An alumina protection tube with an outer diameter of 8 mm and an inner diameter of 6 mm was attached using alumina paste to the top of the thermometer well. About 54.5 g of Fe–C mixture was used as a filler in a pure Ar atmosphere. Pure Fe powder (99.998 %) and C powder (99.9999 %) were purchased from Alfa Aesar. When the powder was completely melted, the crucible and thermometer well were fitted together and then slowly cooled to room temperature. This cell assembly was inserted into an one end closed alumina tube with an inner diameter of 35 mm. Alumina disc plates with a thickness of 0.5 mm were used as radiation shunts; they were supported by 30 mm long alumina tubes. After evacuating the tube to 1.3 Pa, pure argon (99.999 %) with a volume fraction of 0.5 % hydrogen was admitted to the cell. The internal pressure was kept slightly higher than an ambient level [2,4].

A type S thermocouple, which was calibrated at Ag, Cu, Fe–C, and Co–C fixed points, was used to monitor the melting and freezing behavior. The melting emf at the

[1] Protocol for the APMP regional comparison of Co–C eutectic melting point using Pt/Pd thermocouples.

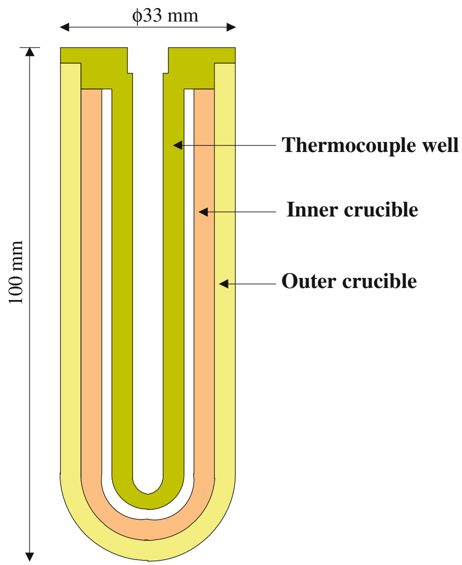

Fig. 1 Schematic diagram of the alumina crucible

Fe–C fixed point with a usual graphite crucible was 11402.3 μV with an expanded uncertainty of 4.7 μV ($k = 2$) [10]. For the melting and freezing tests, we used a vertical furnace with a KANTHAL Super heating element. The temperature was uniform within ±1.0 °C up to a distance of 10 cm from the bottom of the furnace [10]. The melting plateau was obtained at three different melting offset temperatures (+4 °C, +9 °C, and +19 °C) to examine how the melting offset temperatures affect the temperature and shape of the plateau. The freezing tests were performed at a fixed offset temperature of −11 °C. Because the cooling rate can affect the melting temperature of the Fe–C system [4,11], the cooling rate was fixed to $1\,°\mathrm{C}\cdot\mathrm{min}^{-1}$. To examine the reproducibility, we performed a total of 26 melting and freezing tests. During the tests, the furnace temperature was intermittently lowered to room temperature to examine the variation in the melting emf just after cooling to room temperature.

The thermal emf values were measured with a Keithley 2182 nanovoltmeter. A computer-based data acquisition system was used to collect data at 3 s intervals. A conventional ice–water mixture was used to attain the reference temperature at 0 °C. Pure copper wires were used to connect the thermocouple to the measuring device.

3 Results and Discussion

Figure 2 shows the typical melting curves for the melting offset temperatures of +4 °C, +9 °C, and +19 °C. Fairly flat melting plateaus are observed, and the values of the plateau emf are close to each other. The melting plateau becomes shorter as the melting offset temperature increases. This behavior is usually observed in M–C eutectic systems [4]. The melting plateaus were smooth and flat, and therefore allow a calibration of thermometers.

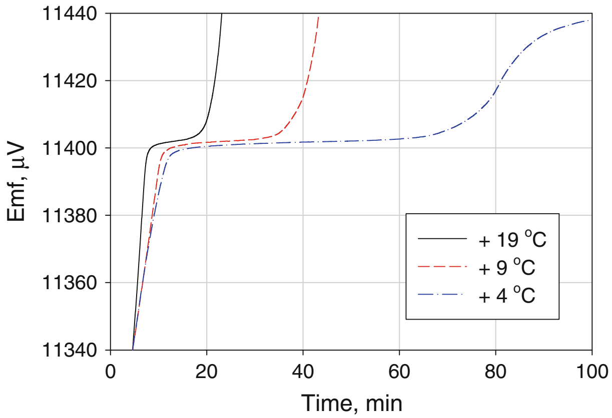

Fig. 2 Variation of the melting curve of the Fe–C eutectic fixed-point cell with offset temperatures (+19 °C, +9 °C, and +4 °C)

The reproducibility of the cell was investigated by performing a number of melting tests at different offset temperatures. Because the main concern was directed on the melting behavior, for the freezes only one freezing offset was used, namely −11 °C below the liquid/solid transition temperature. Table 1 summarizes the measured melting and freezing emf values of 26 realizations. The calculation of the emf which corresponds to the melting temperature was based on the inflection point of the melting plateau, while that of the freezing emf was based on the maximum emf of the freezing curve [3]. The inflection point is defined by the second derivative of the third-order polynomial of the measured emf versus time curve, which is zero at this point. The melting offset temperature was +19 °C for the initial three experiments and +9 °C for the next three runs. Twenty of the melting tests were performed at +4 °C. The furnace temperature was intermittently cooled to room temperature after the 9th, 15th, and 21st freezing experiments so that we could examine how the cooling affects the emf values of the next melting and freezing plateaus. The average melting emf is calculated to 11402.0 μV, which is only lowered by 0.3 μV from that of an Fe–C cell in a graphite crucible [10]. Since we used the same thermocouple and furnace with the previous work [10], the measurement uncertainty of the melting emf of the Fe–C fixed-point cell in an alumina crucible is assumed to be the same as 4.7 μV ($k = 2$).

Figure 3 shows the change in the melting and freezing emf values with the run number. The closed circles denote the melting emf, and the rectangles denote the freezing emf. The melting offset temperatures are indicated in a range, and the downward arrows mean that the furnace temperature was reduced to room temperature. As shown in Fig. 3, the emf of the melts is highly reproducible with a standard deviation of the 26 runs of 0.2 μV (which is equivalent to 0.02 °C), and independent on the melting offset temperatures. However, the freezing emf tends to fluctuate and the average freezing emf is lower than the average melting emf by 14.5 μV (which is equivalent to 1.21 °C). The standard deviation of the freezing emf (1.0 μV) is five times larger than that of the melting emf. After cooling the furnace to room temperature, the emf of the subsequent freezing was slightly higher than the preceding value. In the further

Table 1 Summary of measurements of the melting and freezing emf values of the Fe–C eutectic fixed-point cell at various melting offset temperatures

Experiment no.	Melting transition		Freezing transition
	Offset temperature (°C)	Emf (μV)	Emf (μV)
1	+19	11401.7	11388.2
2		11402.4	11387.3
3		11402.0	11386.3
4	+9	11402.1	11387.6
5		11401.9	11386.7
6		11402.0	11385.6
7	+4	11401.7	11386.8
8		11401.8	11387.0
9[a]		11401.8	11387.8
10		11402.3	11390.2
11		11402.1	11388.1
12		11402.0	11387.4
13		11401.9	11387.2
14		11402.0	11387.3
15[a]		11402.0	11387.3
16		11402.3	11389.6
17		11402.2	11388.5
18		11402.1	11388.1
19		11402.1	11388.3
20		11402.1	11387.2
21[a]		11402.1	11387.1
22		11402.3	11388.5
23		11402.0	11387.7
24		11401.9	11386.8
25		11401.8	11386.1
26		11401.8	11386.0
Average		11402.0	11387.5
Standard deviation		0.2	1.0

[a] After this experiment, the furnace temperature was cooled to room temperature

course of the measurements, the emfs of the freezes gradually decreased but with a tendency to become stable. The literature [4,11,12] confirms that the freezing temperature of Fe–C is sensitive to the freezing offset temperature. The difference we obtained between the melting and freezing temperatures in this work is very close to the results of previous work on a graphite Fe–C cell [4]. Moreover, the melting emf is nearly the same as the value measured for the common graphite Fe–C cell within the uncertainty. Therefore, the melting behavior of the Fe–C eutectic cell of an alumina crucible is nearly identical to the melting behavior of a graphite Fe–C cell.

Figure 4 shows the last five melting and freezing curves at a melting offset temperature of +4 °C and a freezing offset temperature of −11 °C. There was no variation in

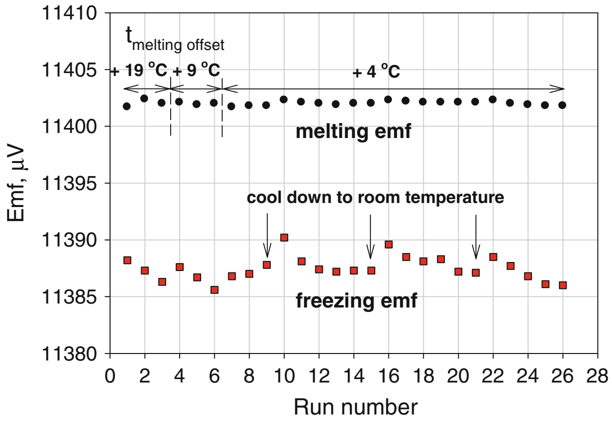

Fig. 3 Summary of emfs measured at the melts and freezes of the Fe–C eutectic fixed-point cell

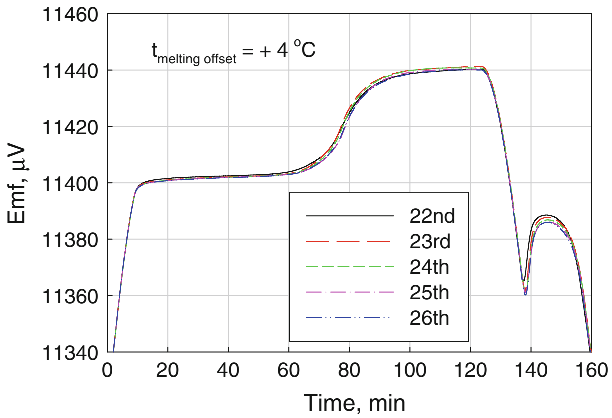

Fig. 4 Last five melting and freezing curves of the Fe–C eutectic fixed-point cell at a melting offset temperature of +4 °C and a freezing offset temperature of −11 °C

the lengths of the melting and freezing curves. The plateau length and the emf values of the melting curves are nearly the same, though a slight change in the freezing emf can be observed. Figure 4 confirms the very good reproducibility of the melting emf of the alumina cell depicted in Table 1 and Fig. 3.

After all the experiments, we visually inspected the cell and found that it was not broken. We conclude, therefore, that the Fe–C eutectic melting point can be realized with a very high reproducibility by using an alumina crucible. The success of the alumina Fe–C cell enables us to study another metal–carbon cell in the higher temperature range. Recently, Pearce et al. [13] reported that pure Pd was found in the graphite thermowell space in a Pd–C fixed point after several times of melting and freezing. This may be due to the diffusion of metallic Pd through the porous graphite wall, and thus it would lead to hypereutectic Pd–C. Since sintered alumina is thought to be denser than graphite, the diffusion of Pd could be prohibited by using an alumina crucible and wall. Thus, we think that it is quite worthwhile to try to make a Pd–C cell using alumina. As an application to another M–C system, a Si–SiC eutectic system will be considered next. Kim et al. found that the Si–SiC eutectic can be a new high-temperature fixed point around 1410 °C [14]. This temperature is critical to calibration of Pt/Pd thermocouples, and also it is possible to replace the expensive Pd–C with economic Si–SiC even though the melting temperature of the Si–SiC eutectic (∼1410 °C) is lower than Pd–C (1492 °C). However, they indicated the possibility of a composition change due to the reaction of Si and C into SiC. This problem can be expected to be overcome by also using alumina crucible. Therefore, it is worthwhile to make Pd–C and Si–SiC fixed-point cells using an alumina crucible, and we aim to develop a new Si–SiC eutectic point for thermocouple thermometry.

4 Conclusions

In this work, we used an alumina crucible to prepare an Fe–C eutectic point for the calibration of a thermocouple. The melting and freezing behavior was investigated through 26 different realizations at various melting offset temperatures (+4 °C, +9 °C, and +19 °C) and at a fixed freezing offset temperature of −11 °C. With a standard deviation of 0.02 °C, the melting emf values are very reproducible and they proved to be insensitive to the melting offset temperatures. Comparing with results obtained for the Fe–C cell contained in a common graphite crucible, melting emfs were quite close to each other within the expanded uncertainty of 4.7 μV (0.39 °C, $k = 2$), only a difference of 0.3 μV (25 mK). Moreover, the cell was found to be unbroken. These results confirm that an alumina crucible is applicable for use with metal–carbon alloys because of the absence of any chemical reaction with the elements. It is proposed that an alumina crucible can be an alternative crucible material to prevent the diffusion of Pd through graphite in Pd–C and the reaction of Si with C into SiC in Si–C system. In our next work, we will endeavor to make another metal–carbon cell (Si–SiC eutectic point) by using an alumina crucible at a higher temperature above 1400 °C.

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