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DEVELOPMENT OF METAL-CARBON EUTECTIC CELLS FOR CONTACT THERMOMETRY AT KRISS

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Abstract: We report the status of development of metal-carbon eutectic cells for contact thermometry at KRISS. Up to now, Co-C, Ni-C, Fe-C and Pt-C eutectic cells have been fabricated and their performance has been tested. The uncertainty of Co-C melting point using a Type B thermocouple was 0.9 °C (k=2). The melting plateau of the Fe-C eutectic cell has shown a dependence on the pre-freezing set temperature.

Keywords: metal-carbon eutectic, thermocouple thermometry, fixed points

1. INTRODUCTION

The International Temperature Scale of 1990 (ITS-90) consists of 17 fixed points and four primary interpolating thermometers [1]. The freezing point of copper (1084.62 °C) is the highest among these fixed points and lies in the regime of the radiation thermometry. Therefore, to ensure the linearity of the temperature scale above the Cu point, additional secondary fixed points at higher temperatures are necessary. The development of such fixed-point cells has been hindered by the unavoidable contamination from the crucible materials which are required to withstand at high temperature.

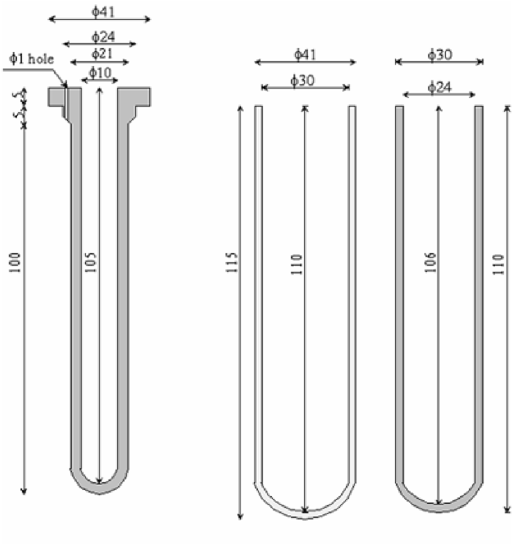
In 1999, Yamada, Sakate, Sakuma and Ono introduced realization of the metal-carbon eutectic cells with the combination of carbon crucibles [2]. The metal-carbon eutectic materials, being alloy of pure metal and carbon, are inherently unaffected by small carbon contamination from the crucible elements. Since then, various metal-carbon eutectic cells have been realized for the use of the radiation thermometry [3]. Furthermore, a new design of the eutectic cells has been made for the use of the thermocouple thermometry [4], which is the most widely-used contact thermometry in practical applications.

In this paper, we review recent activities at Korea Research Institute of Standards and Science (KRISS) regarding metal-carbon eutectic cells for contact thermometry. Cobalt-carbon, nickel-carbon, iron-carbon and platinum-carbon eutectic cells have been successfully realized so far at KRISS and their characteristics around the corresponding eutectic points have been tested using thermocouple thermometry.

2. METHODS

2.1. *Preparation of the eutectic cells*

The crucibles for the metal-carbon eutectic cells were made of graphite from TOKAI Carbon Co. (Japan, Model G348.) The schematic diagram of the graphite crucible and thermometer well for the Ni-C and Co-C eutectic systems can be found elsewhere [5]. For the Co-C and Ni-C eutectic cells, the inner diameter of the crucible was 25 mm and the thickness of the wall was 8 mm. The inner diameter of the thermocouple well was 10.5 mm. For the Fe-C and Pt-C cell, a double-wall structure was employed to minimize damage in case of the breakage of the inner crucible. Figure 1 shows a schematic diagram of the thermocouple well and crucibles for the Fe-C system. The inner diameter of the inner crucible of the Fe-C cell was 24 mm and the thickness of the two walls together was 8.5 mm. The thermometer well and crucibles was similarly designed for the Pt-C cell but the crucibles are thicker. The inner diameter of the thermocouple well was 10.0 mm for the Fe-C cell and 8 mm for the Pt-C cell.



(a) Thermocouple well (b) Outer crucible (c) Inner crucible

Fig. 1. Design of the thermocouple well and the double-wall crucibles for the Fe-C eutectic cell.

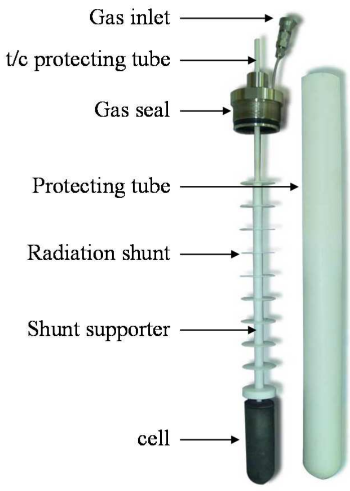


Fig. 2. A representative photograph of the fabricated eutectic point cell for the Co-C, Ni-C and Fe-C.

The volume of the space between the thermometer well and the (inner) crucible, that is to be filled with mixture of metal and carbon, was calculated to be 14.6 cm^3 for the Co-C and Ni-C cells, 11.0 cm^3 for the Fe-C cell and 8.7 cm^3 for the Pt-C cell. High purity metal power (nominal purity of 99.998 % for Co and Fe, 99.996 % for Ni) and carbon power (nominal purity of 99.9995 %) was purchased from Johnson Matthey Co (USA). Platinum powder with nominal purity of 99.999 % was purchased from Tanaka, Japan. About 95 % of the space was filled with the metal-carbon mixture except for the Pt-C eutectic cell that was filled with only about 80 % of its available volume.

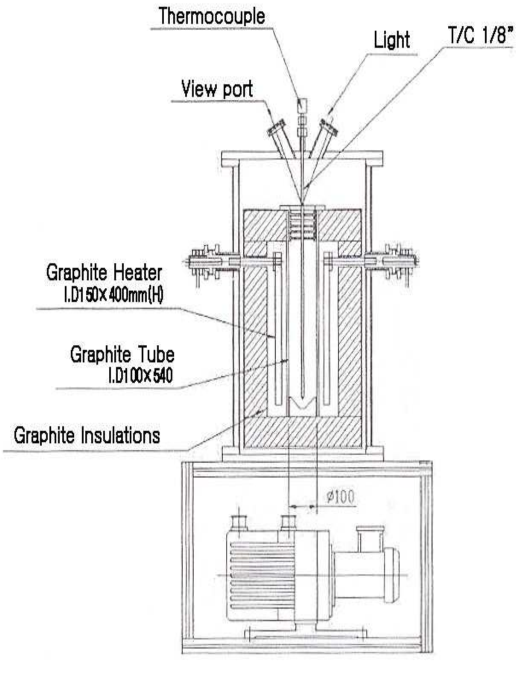


Fig. 3. A schematic diagram of the high temperature furnace built at KRISS.

Figure 2 shows a representative photograph of the eutectic point cell. The filled Co-C, Ni-C or Fe-C cells were inserted into alumina tube as seen on the right side in figure 2. Thermocouple protecting tube was inserted into thermocouple well and radiation shunts were threaded with a shunt supporter. In case of the Pt-C, the overall design was similar except that the material used was graphite instead of alumina and zirconia tube was used for thermocouple protection.

In every process of the cell fabrication for the Co-C, Ni-C and Fe-C cell, as well as during measurements of the transition temperatures, the atmosphere inside the cell was controlled to be slightly above the ambient pressure of argon with 0.5 vol% hydrogen. The whole experiments were performed using a vertical furnace with a Kanthal-super heating element. For the Pt-C cell, a high temperature furnace with graphite as heating element has been built at KRISS and tested up to 2300 °C. Figure 3 shows a schematic diagram of the furnace. The atmosphere inside the furnace while the Pt-C cell was made and its temperature was measured was mostly helium with 0.5 vol% hydrogen.

2.2. Thermocouple thermometry

The temperature of the eutectic cells was monitored by a Type B or a Pt/Pd thermocouple for the Co-C and Ni-C cells and a Pt/Pd thermocouple for the Fe-C cell. The thermocouples were annealed and heat-treated following a conventional procedure [6]. A 1/8-inch tungsten-5%rhenium/tungsten-26%rhenium thermocouple was used for the Pt-C cell. Molybdenum tube was used as a thermocouple sheath. The reference junction was made using usual ice-water mixture and pure copper wires were used to connect from thermocouple wires to the digital voltmeter. The thermal emfs were then measured using a Keithley 2182 nanovoltmeter. A computer-based data acquisition system was used to collect data with 3-second time intervals.

3. RESULTS

3.1. Cobalt-carbon and nickel-carbon eutectic cells

To realize melting and freezing plateaus of the Co-C and Ni-C eutectic plateau, the temperature of the furnace was set to 4 °C (3 °C for Ni-C), 8 °C, 13 °C and 18 °C above the expected transition point to induce melting and to 3 °C, 5 °C, 7 °C and 9 °C below to induce freezing. For each set temperature, the experiment was repeated for more than three times to collect enough statistics for the average plateau emf. Figure 4 shows typical melting and freezing plateau of Co-C eutectic cell for different set temperatures measured by a Type B thermocouple.

In figure 5 the emf values of the melting and freezing plateau of the Co-C and Ni-C eutectic cells are plotted as a function of the difference between the expected phase transition temperature and the furnace set temperature. The average emf and the standard deviations of the emfs expressed as error bars. In both eutectic cells, melting and freezing emfs are affected by the set temperature. In case of melting, a larger temperature difference (higher melting-induce temperature) results in a higher melting emf while in case of freezing, a smaller temperature difference (higher freezing-induce temperature) results in a higher freezing emf. However, the dependence is much weaker in case of the melting than in freezing as indicated as the smaller slopes of the fit lines in both figures 5(a) and 5(b). Therefore when Co-C or Ni-C eutectic systems are used for thermocouple calibrations, the melting plateaus are preferred to the freezing plateau as a fixed point.

Table 1 shows the uncertainty budget of melting plateau of the Co-C eutectic system for a Type B thermocouple [5]. The dominating factor in the uncertainty budge is the inhomogeneity of the thermocouple. The combined uncertainty factor that comes from the cell and the DVM amounts only to 0.07 °C. Therefore, this eutectic cell is characterized to be good enough for calibrations for high accuracy temperature measurement using thermocouples.

3.2. Iron-carbon eutectic cell

The performance of the Fe-C eutectic cell was also tested with a Pt/Pd thermocouple. Figure 6 shows melting (freezing) plateau of the Fe-C eutectic cell for different melting-induce (freezing-induce) set temperatures. The freezing temperature, as well as the duration of the freezing plateau, has a rather large dependence on the freezing set temperature. Comparing figures 6(a) and (b), the melting-induce temperature dependence of the melting plateau is much weaker than the freezing-induce temperature dependence of the freezing plateau, similar to the case of Co-C and Ni-C eutectic systems as seen figures 4 and 5. Therefore it can be concluded for Fe-C eutectic system as well that the melting plateau is preferred to the freezing plateau for the use of the thermocouple calibration.

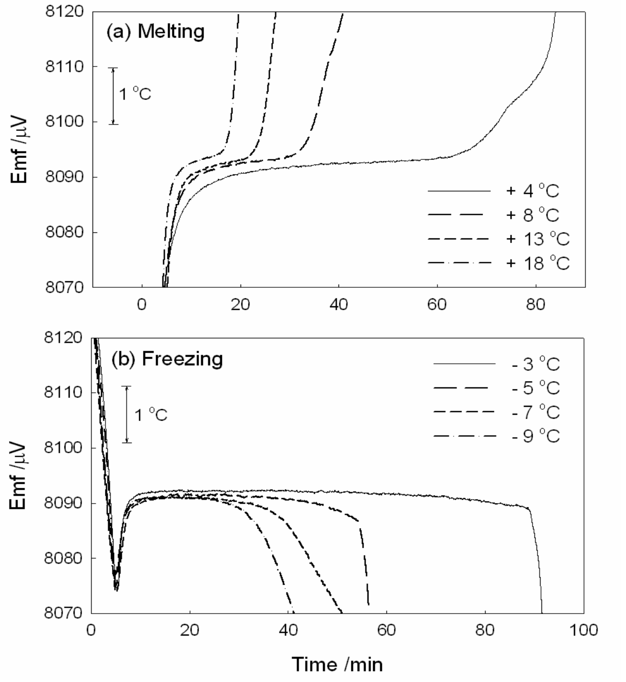


Fig. 4. Typical melting and freezing curves of the Co-C eutectic cell measured by a type B thermocouple.

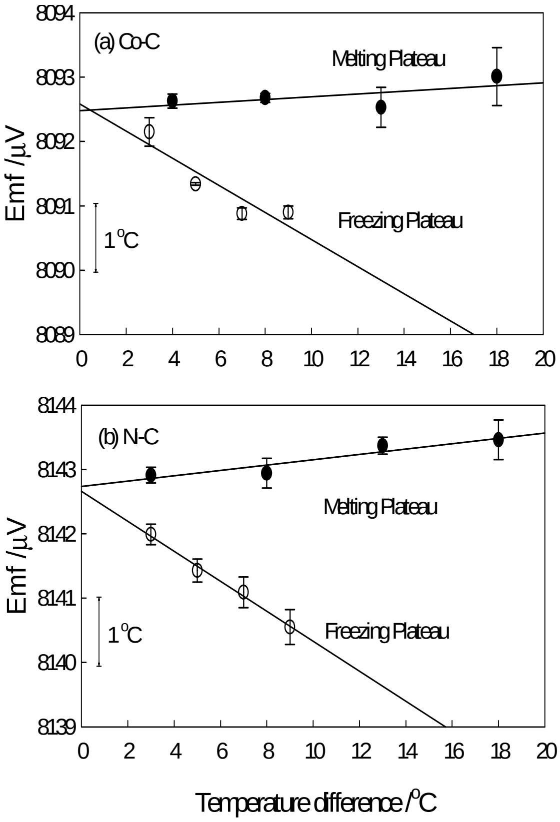


Fig. 5. Emf at the melting and freezing plateaus of the (a) Co-C and (b) Ni-C eutectic cells. The emf values are plotted as a function of the difference between the expected phase transition temperature and the furnace set temperature.

One intriguing fact on figure 6(a) is that the higher melting-induce temperature results in *lower* melting plateau, appearing as opposite to the result of Co-C and Ni-C. However, this can be qualitatively explained by the result of Sasajima, Yamada, Bloembergen and Ono [7] and the sequence of data acquisition in figure 6. The melting plateau when the melting-include temperature of + 2 °C, + 5 °C, + 8 °C and + 10 °C are taken right after the freezing done with a freezing-induce temperature of - 3 °C, -5 °C, -8 °C and -10 °C, respectively. According to the previous report [7], the melting plateau is affected by the pre-freezing rate. Therefore, our melting plateau data might be systematically influenced by the pre-freezing rate that was used right before realizing each melting.

Table 1. Uncertainty budget for the melting point of the Co-C system for a Type B thermocouple

Uncertainty factors	Standard Uncertainty /μV
Factors related to cell and DVM	
Reproducibility	0.06
DVM reading	0.10
Plateau determination	0.58
Deviation from the ideal temperature	0.08
Factors related to the thermocouple	
Thermocouple stability	0.40
Thermocouple inhomogeneity	5.02
Expanded uncertainty (k = 2)	10.2

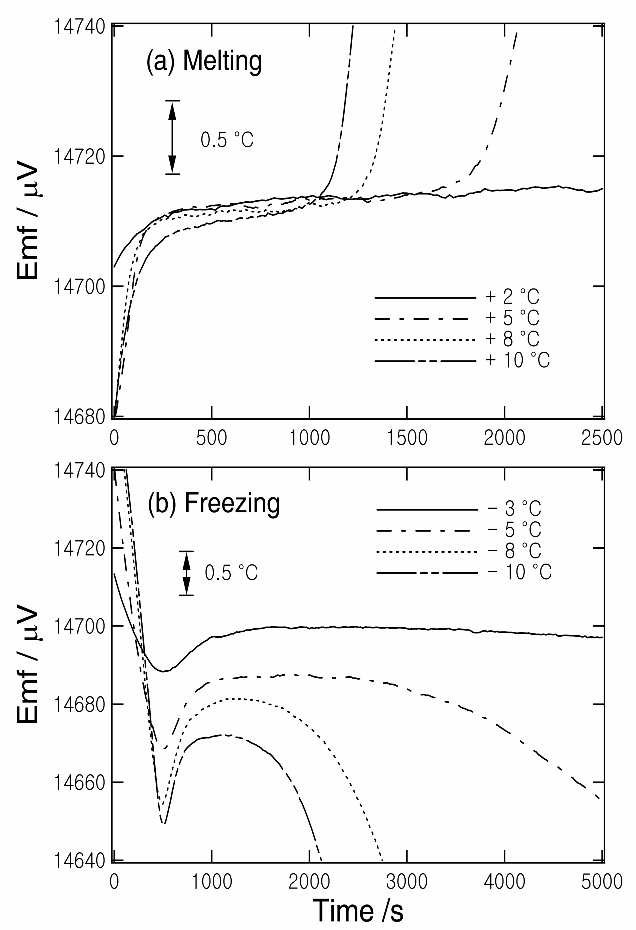


Fig. 6. Typical melting and freezing curve of the Fe-C eutectic cell measured by a Pt/Pd thermocouple.

This effect is further studied using our Fe-C eutectic cell as shown in figure 7. The set temperature for melting was set to 5 °C above the expected transition temperature for all runs but the temperature for freezing prior to each melting was set differently from -3 °C to -70 °C below the expected transition temperature. It can be clearly seen from this result that the slower pre-freezing rate (i.e., smaller temperature difference to induce preceding freeze) results in the higher melting temperature, consistent to the previously reported result [7]. Therefore, it is suggested from this set of experiments that care must be taken for the pre-freezing rate when the *melting* plateau of the Fe-C eutectic system is used for thermocouple calibrations.

In addition to the eutectic transition, the Fe-C alloy also goes through "eutectoid reaction" around 727 °C. As the temperature is raised across the eutectoid temperature, the α-ferrite (solid solution of carbon in BCC iron) transforms to γ-austenite (solid solution of carbon in FCC iron.) Since this eutectoid reaction is also a first-order transition, this can, in principle, be used as a fixed point for the calibration of thermometers. Figure 8 shows the temperature of the Fe-C cell monitored by a Pt/Pd thermocouple around the eutectoid temperature. The transition shows a reasonably good plateau with repeatability less than 0.2 °C even for different heating rate across the eutectoid temperature.

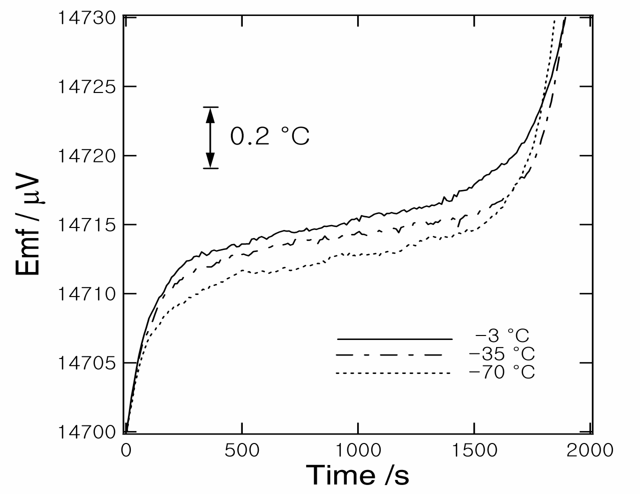


Fig. 7. Melting plateau of the Fe-C eutectic cell for different pre-freezing set temperatures.

However, two problems must be addressed before using the eutectoid transition as a fixed point for calibration. Firstly, the γ-to-α transition shows a much poorer plateau than the α-to-γ transition shown in figure 8. Secondly, there is a rather large temperature difference of ~ 15 °C between the plateau in α-to-γ and γ-to-α transitions (734 °C for the α-to-γ transition and 719 °C for the γ-to-α transition.) While this could be attributed to the fact that the content of carbon in the iron-carbon eutectic alloy is larger than the eutectoid composition, more experiments are needed to resolve these issues. Once these are done, the next logical step is to assign thermodynamic temperature or ITS-90 temperature to the Fe-C eutectoid reaction for the use of thermometer calibration. The use of this transition as a fixed point is especially interesting because two fixed-point measurements that share many experimental conditions in common such as thermocouple inhomogeneity or temperature profile of the furnace can be done. This can potentially very useful in characterizing thermocouples by measuring emf ratio with a very small uncertainty at two distant fixed points.

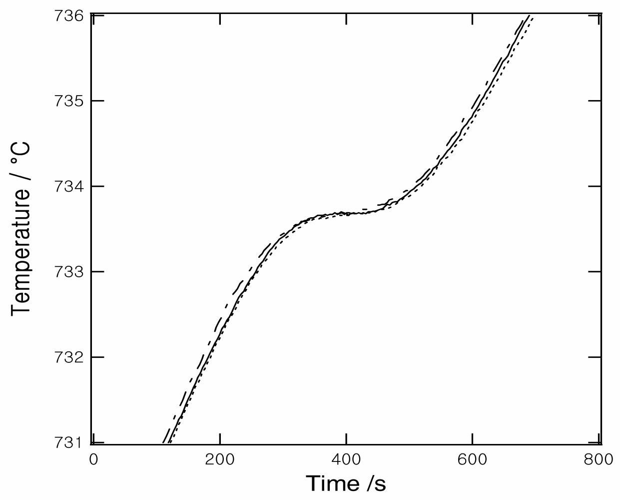


Fig. 8. Temperature of the monitoring thermocouple around the eutectoid transition of Fe-C cell.

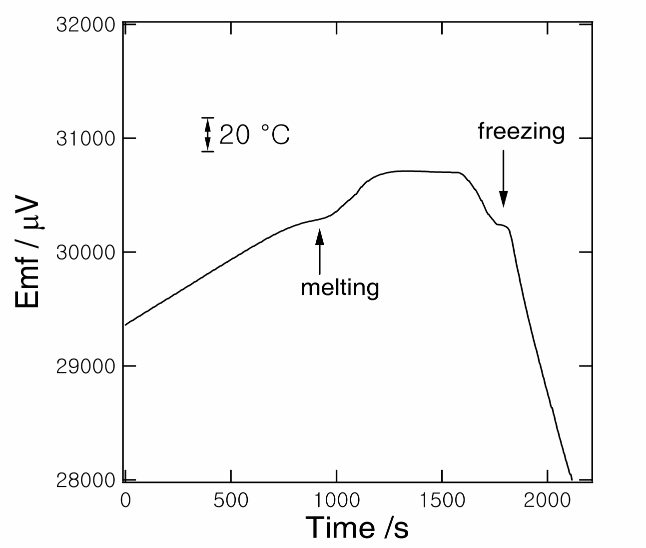


Fig. 9. The melting- and freezing-“plateaus” of a Pt-C cell measured with a W-5Re/W-26Re thermocouple.

3.3. Platinum-carbon eutectic cell

Figure 9 shows the performance of a Pt-C eutectic cell measured with a W-5Re/W-26Re thermocouple. The melting “plateau” is weak showing a slight kink but the freezing plateau is relatively clear. According to the ASTM standard table [8], these plateaus are located at approximately 1740 °C close to the literature value of the Pt-C eutectic point (1738 °C). The difference between the melting plateau emf and the freezing plateau emf corresponds to about 3 °C. The duration of the freezing is about 50 s. Our short-term plan on the Pt-C eutectic point is to find the optimal operating condition to realize best melting and freezing plateaus from this new cell. However, it is believed that the short duration of the freezing plateau as well as the finite slope in the melting “plateau” and the temperature difference between the melting and freezing is due to that the amount of platinum-carbon mixture was too small for the thermal mass of the eutectic cell, thermocouple elements, sheaths and insulating materials. Therefore, our mid-term research plan on the Pt-C eutectic cell is to make a larger Pt-C cell with more platinum-carbon alloy mixture to obtain better fixed-point performance.

5. CONCLUSION

Four metal-carbon eutectic cells, Co-C, Ni-C, Fe-C and Pt-C for contact thermometry have been produced and their performance has been tested at KRISS. The Co-C and Ni-C eutectic cells have very similar characteristics to each other. The uncertainty of the melting point of the Co-C eutectic cell using a Type B thermocouple has been evaluated to be 0.9 °C (k = 2), characterizing this cell good enough for thermocouple calibrations up to 1324 °C. For the Fe-C eutectic cell, the effect of the pre-freezing rate on the melting plateau has been studied systematically. The result indicates that slower pre-freezing rate is followed by a higher melting plateau, consistent to the previously reported result [7]. The most-recently made Pt-C has shown a hint of melting and freezing plateau. However, more experiments are needed to find an optimal sequence of operation for the Pt-C eutectic cell for thermocouple calibrations. This would extend the calibration range of thermocouples at KRISS to 1738 °C. This would also accomplish better accuracy and ensure the linearity in the calibrations of thermocouples.

At KRISS, a vertical high-temperature furnace has been built for the use of the fixed-point cells above 1700 °C. The furnace has been tested successfully up to 2300 °C and used for the fabrication and initial test for the recently-made Pt-C eutectic cell. Using this high-temperature furnace, a project is under way to fabricate and use a Rh-C eutectic cell and another Pt-C cell with a better fixed-point performance for the contact thermometry.

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