Determination of Eutectic Melting Phase Transition Temperature of Metal-Carbon Eutectic Fixed Points

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Abstract. International Temperature Scale- 1990 (ITS-90) is formulated based on various phase transition temperatures of high pure substances to cover the temperature range from 0.65 K to 1357.77 K (-272.5 °C to 1084.62 °C), where kelvin is defined on triple point of water (TPW) at 273.16 K and the higher defined fixed point is freezing point of copper at 1357.77 K. To extend the temperature scale at higher temperatures, metal-carbon eutectic fixed points areextensively being developedas the reference standardsupto 3000 °Cfor thermometry and radiometry applications. The assignment of the eutectic melting transition temperatures to these metal-carbon eutectics is challenging as the melting plateaus are not as flat and wide as the conventional high pure metal fixed points. This paper presents the method to determine eutectic melting transition temperature by calculating inflection point for Fe-C and Co-C eutectic fixed point cells developed at CSIR-NPL, the national metrology institute (NMI)of India. The noble metal Type-S thermocouple calibrated on ITS-90 fixed points was used to measure and determine the melting transition temperatures of Fe-C and Co-Ccells, and the associated uncertainties in determination of transition temperatures were evaluated.

INTRODUCTION

Temperature is an intensive property of matter and kelvin (K) is one of the seven base units. Therefore, the precision measurement of temperature is required at different temperature ranges, as the measurement uncertainty levels considerably propagate below and above the range from its definition at TPW (0.01 °C) temperature [1]. Platinum resistance thermometers (PRTs) are the reference thermometers in the range from -196 °C to 962 °C, thermocouples in the range from 0 °C to 1600 °C and pyrometers/thermal imagers can be used as high as 3000 °C. CSIR-NPL, NMI of India, has established the overall facility in thermometry from – 200 °C to 3000 °C, 10 % to 95 % RH and -30 °C frost point to 50 °C dew point, and disseminating the thermometry traceability to Indian and SAARC users through precision calibrations. Since the introduction of metal-carbon (M-C) eutectic fixed point in 1999 [2-3] for high temperature applications, various NMIs have reported the development of metal-carbon eutectic cells with repeatable and reproducible results [4]. The successful development of these fixed points has facilitated withreduced uncertainty of measurement and created a pathway for Metrologists to overcome the difficultiesin determining temperature by extrapolating temperature scale above 1100 °C.Further, high temperature M-C eutectic temperature fixed points are developed and realized both by contact and non-contact thermometry.

In this paper, we report the development of Fe-C [1153 °C] and Co-C [1324 °C] for contact thermometry and realized using the ITS-90 calibrated Type-S thermocouple (Pt/ Pt-Rh-10%). The next step after realization is to determine temperature of eutectic melting plateau of these cells, where the plateaus are not as flat and wide as the high pure metal melting/freezing transitions [5]. The plateau of the M-C eutectic melting transition has slightly increasing tendency due to interface energy between facetingcarbon and non-faceting metal rich phase [6]. To determine the melting temperature of M-C eutectics many methods have been reported [6, 7], out of which, the

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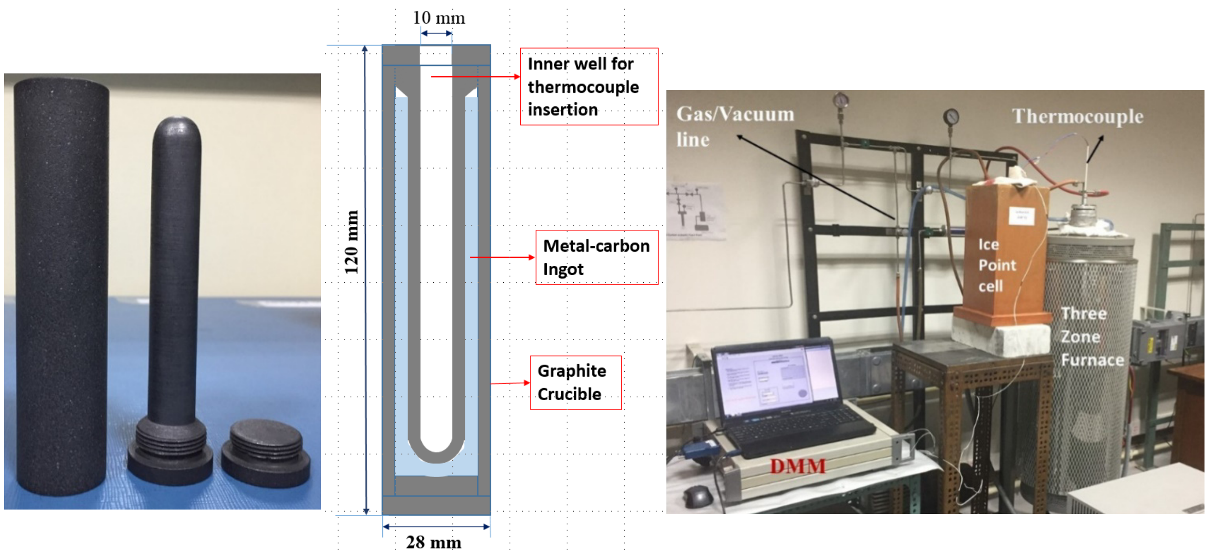
point-of-inflection(POI) method is widely used. In this paper, we report the detailed analysis of determination of melting transition temperatures of indigenously developed Fe-C and Co-C fixed point cells by using POI method.

EXPERIMENTAL

The high pure graphite was machined to form the graphite crucible as shown in Fig 1 (a) and (b), designed to incorporate the minimum use of high pure metals while giving sufficient immersion depth of about 11 cm for the thermocouple. The 4.15 wt % of 99.9995 % pure graphite powder as a source of carbon was added to 99.998 % pure iron powder, and 2.4 wt % in 99.998 % pure cobalt powder to form Fe-C and Co-C eutectic mixtures, respectively [8, 9]. The cell was placed into the high pure recrystallized alumina tube, with graphite and ceramic wool sequential thermal shields and sealed with water jacketed assembly head. The cell assembly was placed in three-zone tube furnace, as shown in Fig. 1 (c), and maintained at 1 atm pressure of 5N Pure Argon gas. The calibrated Type-S thermocouple and 8 ½ DMM (0.01 µV) were used for the realization of phase transition temperature.

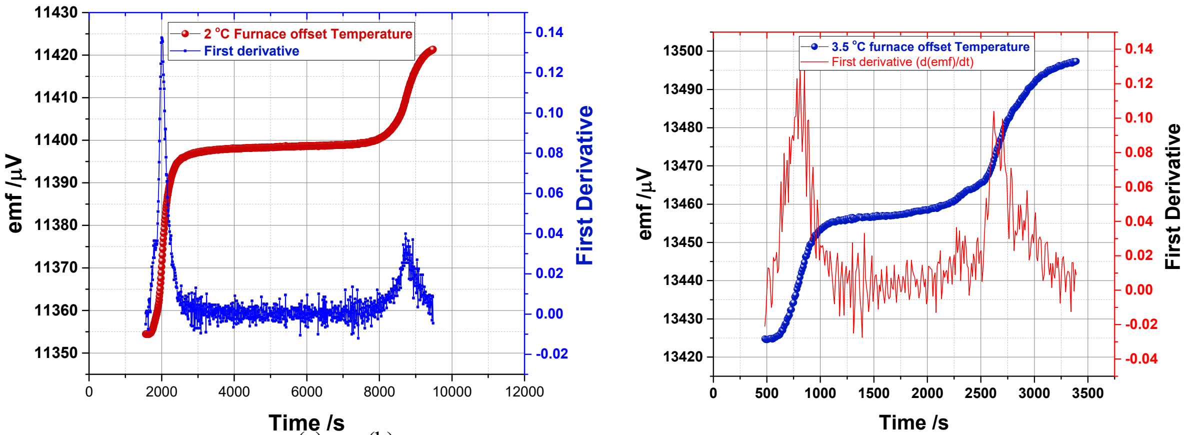


(a) (b)(c)

FIGURE 1. (a) Photograph of the graphite crucible, (b) schematic M-C cell and (c) Measurement set-up for the realization of the Fe-C and Co-C eutectic cell.

RESULTS AND DISCUSSION

For the realization of Fe-C and Co-C eutectic fixed point cells, furnace temperature was set to 5 ^{o}C below the theoretical eutectic transition temperature at 1 atm pressure of argon inside the cell. The cells were kept at this temperature for 2 h until the cell temperature comes in equilibrium with the furnace temperature. Subsequently, the furnace temperature was increased by 1 ^{o}C per minute to furnace offset temperature of 2 ^{o}C above eutectic transition temperature of Fe-C [1153 ^{o}C], as shown in Fig. 2 (a). Initially, temperature of Fe-C cell and hence the emf of realizing thermocouple rises as per specific heat and at the melting transition it remains constant until it received the latent heat energy required for the complete melting phase transition from solid Fe-C eutectic ingot. The distinct and long duration melting plateau suggest that the phase-pure Fe-C has been formed. The first derivative or constant gradient of melting plateau also depict the eutectic phase transition of Fe-C, without forming the hypo- or hyper-eutectic phase. Similarly, Co-C eutectic cell was subjected at 3.5 ^{o}C furnace offset temperature and long melting plateau was achieved, as shown in Fig. 2(b). The duration of the plateau depends on offset temperature of furnace, mass of the ingot and the latent heat required for the complete phase transitions. The clean melting plateaus govern that the metrological grade M-C cells have been successfully formed and further evaluated for their metrological characterizations to determine the melting transition temperatures and the associated uncertainty.



(a) (b)

FIGURE 2. (a) The Fe-C melting plateau and its gradient d(emf)/dt plot measured at 2 °C furnace offset temperature (b) The Co-C melting Plateau and gradient d(emf)/dt plot measured at 3.5°C furnace offset temperature by Type-S TC.

To determine the melting transition temperature using POI method for Fe-C, the melting curve was fitted by the 3rd order polynomial followed by first and second derivatives. At the inflection point the first derivative shows minima and second derivative has zero value. The equation of the fitted curve can be written as:

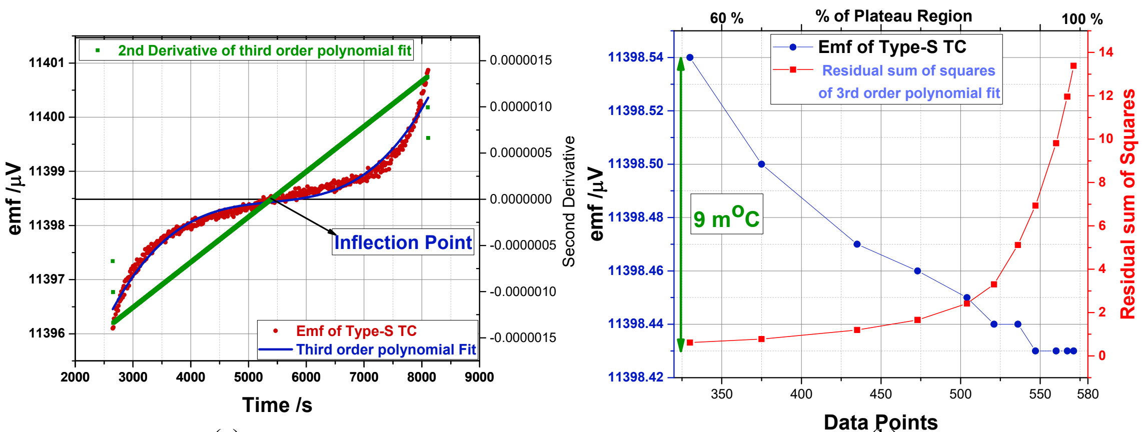
$$emf = At^3 + Bt^2 + Ct + D,$$

$$\frac{d(emf)}{dt} = 3At^2 + 2\mathrm{Bt} + \mathrm{C} \quad , \quad \frac{\mathrm{d}^2(\mathrm{emf})}{\mathrm{d(t)}^2} = 6At + 2B$$

$$\textit{At inflection point:} \quad \frac{\mathrm{d}^2(\mathrm{emf})}{\mathrm{d(t)}^2} = 0$$

So the inflection point was determined to be at t = -B/3A, The Fig. 3 (a) showsthe third order polynomial fit with second derivative plot, the intersection point of polynomial fit and double derivative is the inflection point of the melting plateau of Fe-C cell.However the POI depends on the selection of plateau width, as the initial surge before plateau depends on the furnace ramping rate, specific heat and pre-melting due to disordered regions between grains [6], and the final rise depends on furnace offset, mix-phase melting and thermocouple response time. The selection of the melting plateau could be different for different users and cells, therefore, the dependency of the inflection on selection of melting plateau region is shown in Fig. 3(b). The "residual sum of squares" decreases with reduction of numberof data points, which indicates that the polynomial fitting gets better with reduction of number of data points, but there is change in POI estimates, depicting that sufficient data range is required to get the consistence POI and hence the emf output of the thermocouple. The change in inflection point is found to be 9 m°C. The temperatures corresponding to the emf of POI of Fe-C (11398.46 µV) and Co-C (13457.01 µV)were estimated to be 1153.33 °C and 1323.85 °C, by referring the calibration table of Type-S Thermocouple at CSIR- NPL used for the realizations.

We have also determined the expanded uncertainty in the realization of melting transition temperatures of Fe-C and Co-C cells by applying the repeatability of melting plateaus as Type-A contributions, and other Type-B components such as uncertainty due to determination inflection point, inhomogeneity of thermocouple, due to heat flux, DVM calibration, thermocouple instability, due to cold junction were evaluated in details, as presented in [9, 10]. The uncertainty thus evaluated is 0.25 °Cand 0.53°C(k=2), respectively, for Fe-C and Co-C cells.



(a) (b)

FIGURE 3. (a) Determination of inflection point by 3rd order polynomial fit and 2nd derivative plot for 95 % plateau, (b) The variation of inflection point and residual sum of squares with number of data points/percentage plateau region for Fe-C cell.

CONCLUSION

The Fe-C and Co-C eutectic fixed point cells were successfully developed at CSIR-NPL with indigenous design and development efforts. The stable, long and repeatable melting plateaus suggest the suitability of M-C cells as reference temperature fixed point cells. Thepresent study reveals that the determination of eutectic melting phase transition temperature depends on the selection of the melting plateau width for the 3rd order polynomial fit. Also, the fitting parameter and selection of plateau regionwere optimized to get the better fit and consistence inflection point value. However, it is found to have very small dependency on the plateau region selection which is 9 m^{o}C for the variation plateau region from 100 % to 60 % for Fe-C cell. Uncertainty in realization by Type-S TC of melting transition temperature of Fe-C was evaluated as 1153.33 ^{o}C ±0.25 ^{o}C, and for Co-C as 1323.85 ^{o}C ± 0.53^{o}C.

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