SICE Annual Conference 2015
July 28-30, 2015, Hangzhou, China

Determination of the Inflection Point of the Co-C HTFP Melting Curve by a Statistical Method

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Abstract: The inflection point (POI) of the HTFP melting curve has been mainly applied as a reference point in comparisons of local temperature scales. It has also been proposed to serve as a lower limit to be set to the liquidus temperature. In this paper, we confine ourselves to the determination of the inflection points by a statistical method for the Co-C involved in InK-WP1. Details of the metod will be introduced in this paper.

Keywords: HTFP, statistical method, inflection point

1. INTRODUCTION

The discovery of fixed points based on the eutectic transition temperature of particular alloys of metals and graphite (high temperature fixed points – HTFPs) in 1999[1] triggered a huge amount of innovative scientific research into HTFPs under the auspices of the *Consultative Committee for Thermometry*(CCT) [2]. Three metal carbon eutectic systems have been singled out for detailed study by the CCT; Co-C (1324 °C), Pt-C (1738 °C) and Re-C (2474 °C), and have been shown to be robust, repeatable and reproducible [3]. The temperatures of these will be recommended as reference values to the CCT in mid-2015 through a multi-partner measurement campaign coordinated by the National Physical Laboratory (NPL), UK, through the European Metrology Research Programme (EMRP) project Implementing the new Kelvin (InK) [4,5].

In addition, once their thermodynamic temperature has been established, HTFPs are proposed as a means of disseminating a high temperature alternative to ITS-90, within the *mise en pratique* of the definition of the kelvin (*MeP*-K).

NIM, as a non-funded participant of InK, will play a role in InK-WP1, producing a template that determines the inflection point, the liquidus temperature -for melting temperature for the HTFPs involved, allowing the data analyzing process to be unified..

Although the POI is not expected to have any particular significance it has proved so far to be very repeatable and to have great utility for comparison measurements.

Thus far the inflection point (POI) of the melting curve has been mainly applied as a reference point in comparisons of local temperature scales. It has also been proposed to serve as a lower limit to be set to the liquidus temperature of the HTFP T assignment.[6,7]

In this paper, we confine ourselves to the determination of the inflection points of the melting curves for the Co-C HTFP involved in InK-WP1.

In the CCT-WG5-WP2 protocol the uncertainty associated with the POI is estimated by taking the average of POIs, determined for various lengths of the smoothed melting curve. Especially when the melting range is relatively large and the melting curve is not

smooth, the POI can differ (i.e. jump from one POI to another) depending on its derivation procedure. To determine this source of uncertainty, the melting curve is firstly smoothed by taking the moving average with a certain initial averaging length and the inflection point is determined. Then the averaging length is doubled, and the POI is again determined. Finally, the averaging length is halved and the POI is determined again. The standard deviation of the three determined POI is evaluated. The average of the standard deviation for three or more melting curves taken within the same day is derived and is taken as the uncertainty related to the identification of the POI. The requirements for the identification of the POI to be eligible for the definitive thermodynamic temperature measurement were 10 mK for Co-C, 20 mK for Pt-C and 30 mK for Re-C.

However, the fitting range remains ambiguous. We found out that the POI is also sensitive to the fitting range, and can be of 10 mK level even if the residual of the fit is quite small. Thus currently InK practically suggest participants use the middle of the melting plateau to fit, even lack of physical or mathematical meanings. This, identification of the fitting range, should be seriously considered as an uncertainty component associated with the identification of the POI.

2. THE STATISTICAL METHOD

Therefore a statistical method was adopted to determine the inflection point of the HTFP melting curve. The method can be described as follows.

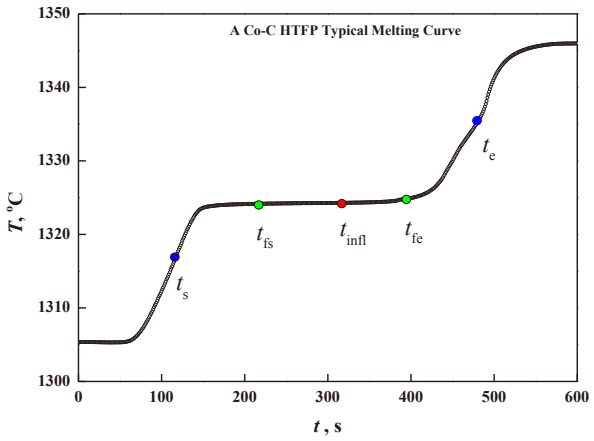


FIG1 A typical Co-C melting curve

The core region of the temperature curve was carefully chosen as $t_s \le t_{fs} < t_{fe} \le t_e$, see Fig1. The t_s and t_e were defined as the beginning and the end of the melting process, and were obtained as the two points of maximum curvature (i.e. zero cross points of the third derivative). Then the start of the fitting range was chosen between (t_s, t_{fs}), and its end was chosen between (t_{fe}, t_e). Thus the total number of the fitting cases was (t_{fs}-t_s)* (t_e-t_{fe}). The corresponding POI of each case was obtained by a third order polynomial fitting.

The fitting procedures were carried out by the Levenberg-Marquardt algorithm, and the statistical distributions of the calculated POIs were characterized by a gaussian distribution, as shown in FIG2.

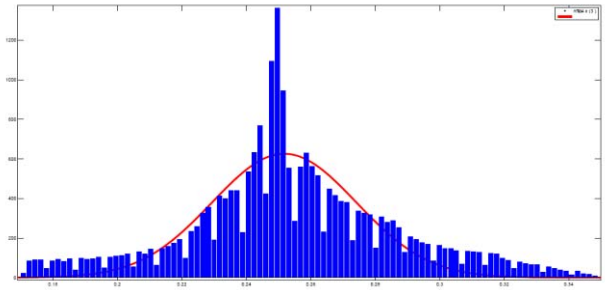


Fig.2 A gaussian distribution fit of the probability of the calculated POIs

Two statistic variables were used: The max value of the distribution was obtained to determine the final POI value and the variance of the distribution was used to describe the accuracy of the method.

Subsequently t_{fs} and t_{fe} were varied by iteration with fixed steps, so that a set of POIs and variances were obtained.

A stop criterion can be set to the iteration process, provided the POI and associated variance show satisfactory convergence.

3. RESULTS AND DISSCUSSION

A NPL Co-C (Co-Fe-A) was realized in a 3 zone furnace. The furnace step for cell realization was set at -10 K for freezing and +25 K for melting, and the melting curve was shown in FIG3

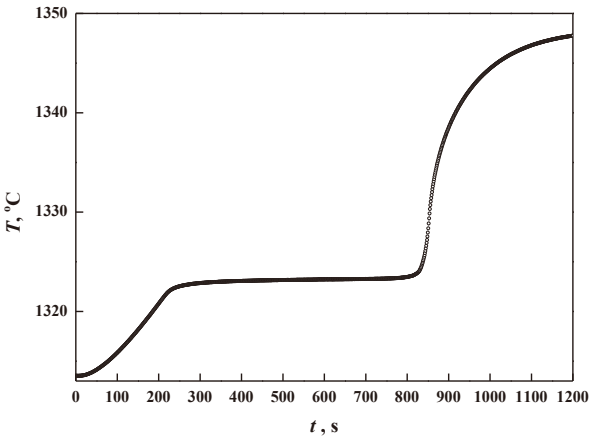


FIG3 The Co-C melting curve used in the analyze

3.1 Conventional Method

According to the defination of the beginning and the end of the melting plateau in section2, the t_s and t_e were obtained as 200 s and 854 s respectively. With respect to the InK protocol, the POI can be obtained by a cubic function fitted to the central half of the melting plateau, i.e. here from 364s to 692s. To get the uncertainty of the identification of the POI, the averaging length were chosen as 5, 10, 20. The POI was calculated as 1323.20 ℃, with an uncertainty 0.01℃(k=1).

3.2 Statistical Method

The initial values of t_{fs} and t_{fe} were set as same as the conventional method, which were 350s and 704s respectively. According to the method in section2, 22500 fitting cases were calculated, the probability of the calculated POIs were ploted in FIG4. From FIG4, the POI can be obtained as 1323.20 ℃, with an uncertainty 0.02℃(k=1).

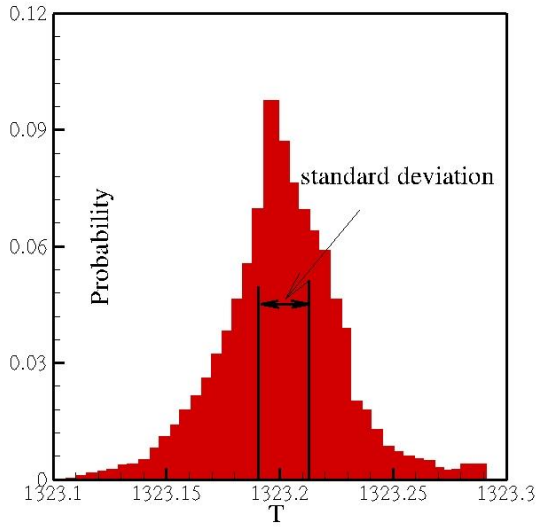
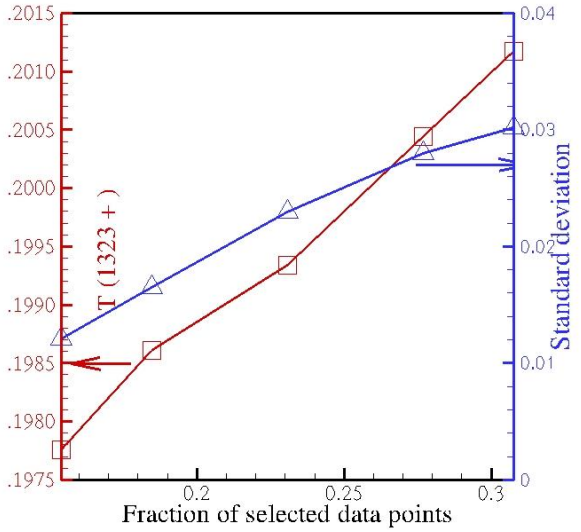


FIG 4 The probability of the calculated POIs for a NPL Co-C realized in a 3zone furnace.

The covergence of the method were checked by varying the start and end of the fitting range, the iteration step was fixed as 50s. The POI and associated variance were plotted in FIG5, which show satisfactory convergence.



The results proved that the statistical method, proposed, is robust and can generate the POI with low uncertainty.

The POI deviations between the conventional and statistical method are significantly less than the uncertainties ascribed by the individual method. This indicates that the POI as obtained by the two methods are in good agreement.

4. CONCLUSION

According to the findings of this study it is recommended that the POI continue to be used as a pragmatic defination of temperature. And the InK proposed practical conventional method can be continuelly adopted.

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