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Certification of reference materials of Alumel, nickel and iron for Curie point

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Abstract The temperature of thermogravimetric analyzer (TG) was commonly calibrated by the reference material of ferromagnetic for Curie point (T_c). RM for T_c was used to be determined by simultaneous thermal analyzer (STA). Three certified reference materials (CRMs) including Alumel, nickel and iron were developed. Prior to the certification, the effects of the heating rate, the magnetic field strength and the type of sample pan upon T_c were investigated using STA and TG. These CRMs were certified by an optimized STA method in a collaborative study with eight laboratories involved. Subsequently, their certified values (expanded uncertainties) were 153.9 °C (1.1 °C), 358.7 °C (1.3 °C) and 771.4 °C (1.5 °C), respectively.

Keywords Curie point · Reference materials · Uncertainty · Thermogravimetric analyzer · Simultaneous thermal analyzer

Introduction

Thermogravimetric analyzer (TG) measures the mass of a sample as a function of time or temperature, which could be employed to quantify the temperature of decomposition, volatilization and oxidation as well as the content of the moisture, volatile components and residues. TG was also used to determine the content of the amorphous carbon and the purity of carbon nanotube [1]. The accuracy and consistency of these results depend on the accuracy of temperature of TG. The determination of the rate of reactions, such as decomposition and volatilization, by using TG also needs an accurate temperature [2]. The temperature of TG was traditionally calibrated using the reference materials (RMs) of ferromagnetic for Curie point (T_c) due to the convenience and repeatability [3].

In 1981, the International Confederation for Thermal Analysis (ICTA, now the International Confederation for Thermal Analysis and Calorimetry, ICTAC) developed a series of RMs for Curie point including metals and alloys (referred as GM 761 below) and determined their T_c by TG in a collaborative study [4]. This series of RMs covered a range of Curie point of 266–754 °C with a range of standard deviation of 5.4–11 °C [4]. In 1987, Charsley et al. [5] employed the simultaneous thermogravimetry and differential thermal analysis (TG/DTA), namely simultaneous thermal analyzer (STA), to determine the Curie point of ferromagnetic. The temperature of the STA was calibrated by the melting point of metals using the DTA curve. And then the STA was used to determine the Curie point of ferromagnetic using the TG curve. By using the STA, the temperature of Curie point traced to SI unit of temperature through the melting point of metals. In 2003, ICTAC developed the second series of RMs for Curie point (referred as ICTAC-2 below) and determined their standard values by the simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC), namely simultaneous thermal analysis (STA), in a collaborative study [6]. The ICTAC-2 including two metals and four alloys covered a range of temperature of 152–1116 °C with a

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standard deviation of 1.0–3.7 °C. The ICTAC-2 RMs were distributed by TA Inc. (DE, USA) now. Other instrument manufacturers, such as PerkinElmer and Netzsch, also provided their own RMs for Curie point. However, there are notable biases among different series of RMs [7].

Up to now, the STA method for T_c remains to be explored for better accuracy. And the certified reference materials (CRMs) for Curie point owning an accurate certified value and a reliable uncertainty were urgently needed. In the present study, three CRMs for Curie point, including Alumel, nickel and iron, were developed and certified by an optimized STA method in a collaborative study.

Experimentals

Materials

Alumel wire was from Omega Engineering Inc. (Norwalk, CT, USA). Nickel powder (CAS 7440-02-0) with a purity of 99.99% and iron powder (CAS 7439-89-6) with a purity of 99.5% were from Sigma-Aldrich Inc. (St. Louis, MO, USA). Each raw material was packaged into 200 bottles with more than 10 g in each bottle. Eight, ten and six bottles were randomly selected for the certification in the collaborative study, the homogeneity test and the stability test, respectively.

CRMs of metals for melting point, including indium (LGC 2601), tin (LGC 2603), zinc (LGC 2609), aluminum (LGC 2612), were from LGC Inc. (Teddington, Middlesex, UK). CRM of Silver for melting point (SRM 1746) was from National Institute of Standard and Technology of USA (Gaithersburg, MD, USA).

Instruments

The Curie point of candidates of CRMs was determined by STAs from three instrument manufacturers, including STA 8000 (PerkinElmer Inc., MA, USA), Q600 (TA Inc., DE, USA) and TGA/DSC1 (Mettler-Toledo Instrument Inc., Greifensee, Switzerland). Pyris 1 TGA (PerkinElmer Inc., MA, USA) was employed to investigate the effects of the heating rate and the magnetic field strength upon Curie point.

Measurement method

Certification method by STA

The candidates of Alumel and iron were determined using the internal standard of temperature. The Alumel wire was cold-rolled into sheets and then cut into pieces of (2–3) mg. 10 mg of Alumel and 1 mg of indium sealed in the aluminum pan were measured. Indium was employed as the internal standard of temperature. 10 mg of iron, 1 mg of aluminum and 1 mg of silver placed in the alumina pan were measured. Aluminum and silver were employed as the internal standard of temperature. Since zinc, nickel and aluminum can form the alloy and simultaneously release heat at the melting point of zinc, the candidate of nickel was determined using tin and zinc as the external standard of temperature. 1 mg of tin and 1 mg of zinc sealed in the aluminum pan were measured. Then, 10 mg of nickel sealed in the aluminum pan was measured.

The heating rate was 10 °C per min. Several NdFeB magnet discs were placed on the top of sample holder outside the furnace. The distance between the magnet discs and the furnace was adjusted to make the change of the apparent sample mass induced by the magnetic force close to 5% of the original value. The flow rate of the carrier gas of nitrogen was about 100 mL per min. The extrapolated initial melting point, namely onset point, was obtained from each DSC curve and was used as the measured melting point of metals (T_m). The extrapolated end Curie point, namely the intersection of the tangent of rising edge and the extrapolated baseline after Curie transition in TG curve, was used as the measured Curie point (T_c).

Measurement method by TG

10 mg of nickel placed in a platinum pan was measured by Pyris 1 TGA. A U-shape Teflon holder containing eight small magnet rods was placed outside the vertical quartz furnace of Pyris 1 TGA. The U-shape Teflon holder was moved up and down to adjust the change of the apparent sample mass.

Results and discussion

STA curves of Alumel, nickel and iron

The STA curves consisting of the TG and the DSC curve of Alumel and indium by PerkinElmer STA 8000 are shown in Fig. 1. The apparent sample mass suddenly increased around 150 °C. Since Alumel transited from the ferromagnetic state to the paramagnetic state at 150 °C, the force exerted by the magnetic field was lost. It was found that the repeatability and reproducibility of endset Curie point are better than those of onset Curie point or inflection Curie point, which is consistent with the results of Garn et al. [4]. In Fig. 1, the measured T_c of Alumel is 152.28 °C and the measured T_m of indium is 155.35 °C. Since the certified melting point of indium (LGC 2601) is

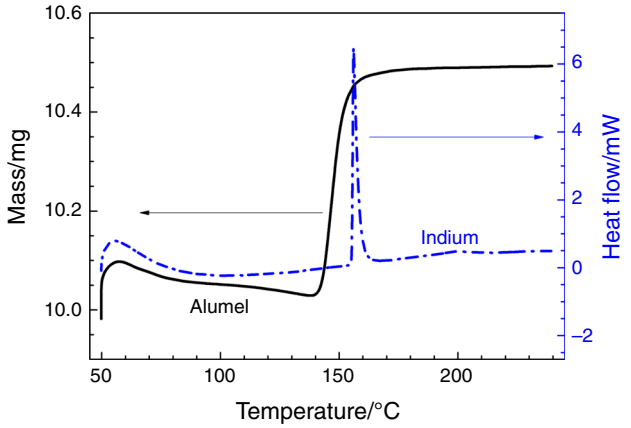

Fig. 1 Curve of temperature–mass–heat flow of Alumel and indium by STA 8000

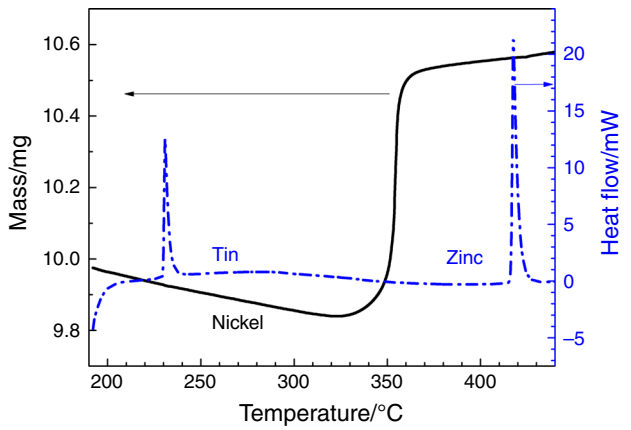

Fig. 2 Curve of temperature–mass of nickel and the curve of temperature–heat flow of tin and zinc by STA 8000

156.60 °C, the modified Curie point (T_c') was 153.53 °C. The TG curve of nickel and the DSC curve of tin and zinc by PerkinElmer STA 8000 are shown in Fig. 2. The STA curves consisting of the TG curve and the DSC curve of iron, aluminum and silver by the same instrument are shown in Fig. 3. The Curie point of ferromagnetic was traceable to SI unit of temperature through the CRMs of metals for the melting point.

Effect of heating rate

Figure 4a–c shows the T_c of nickel at varied heating rates (from 1 to 20 °C min^{-1}) by using STA 8000, TGA/DSC1 and Pyris 1 TGA, respectively. T_c by STA varies with the heating rate (Fig. 4a, b). T_c by STA 8000 had a trend of increasing firstly and decreasing afterward with increasing heating rate. The difference of T_c between a heating rate of 1 °C min^{-1} and that of 10 °C min^{-1} was merely 0.18 °C. At the same time, T_c by TGA/DSC1 decreased with increasing heating rate. The difference of T_c between a

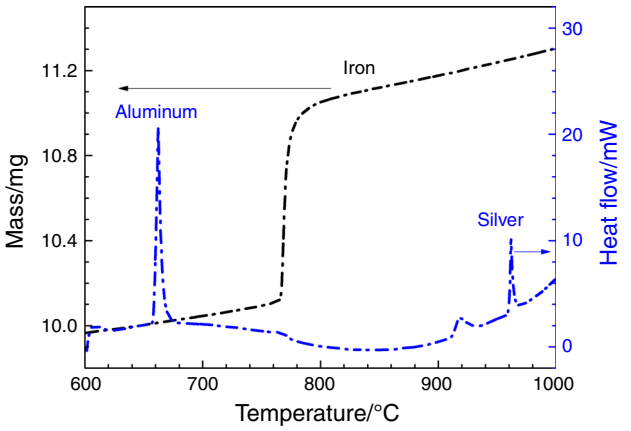

Fig. 3 Curve of temperature–mass–heat flow of iron, aluminum and silver by STA 8000

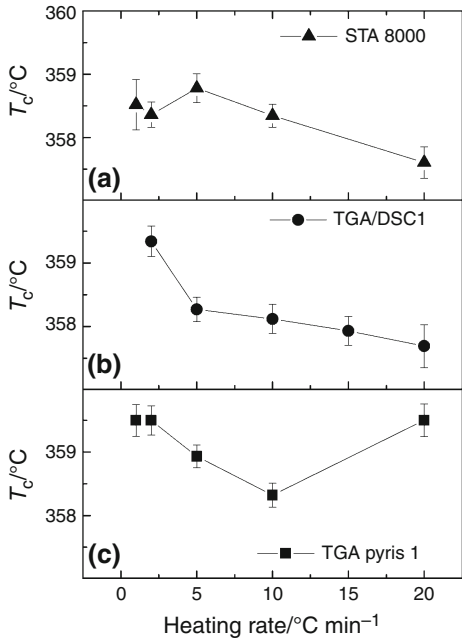

Fig. 4 T_c of nickel at varied heating rate by STA 8000 (**a**), TGA/DSC1 (**b**) and Pyris 1 TGA (**c**)

heating rate of 2 °C min^{-1} and that of 10 °C min^{-1} was 1.22 °C. T_c by Pyris 1 TGA decreased firstly and increased afterward with increasing heating rate (Fig. 4c).

Gallagher et al. [6] investigated the effect of the heating rate on T_c by using nine types of STA from different instrument manufacturers. They found that for most of the STA, T_c varied slightly with the heating rate, and the effect of the heating rate on T_c differed with the instrument manufacturer [6]. Therefore, the average of different rates was used as the measured value of T_c by individual laboratory [6].

STA had been calibrated by using the internal standard or the external standard; therefore, the effect of the delay of

the thermocouple on T_c was reduced. However, the delay of the balance, as well as the slightly temperature difference between the ferromagnetic and the internal standard in the temperature gradient, might result systematic errors of T_c. Since all these errors increase with the heating rate, they could be reduced by using a low heating rate theoretically. Some candidates of CRM, such as iron in powder, are readily oxidized at high temperature; therefore, the low rate should be avoided. Determination by the fitting and extrapolation of the data of T_c versus heating rate is time-consuming and thus is not applicable for the collaborative study. Therefore, the candidates of CRMs were determined at a heating rate of 10 °C min^{-1}.

Effect of magnetic field strength

The effect of the magnetic field strength on T_c was investigated as shown in Fig. 5. The magnetic field strength applied to the ferromagnetic sample in TG or STA is difficult to be measured. Since the magnetic force applied to ferromagnetic sample is proportional to the magnetic field strength, the change of the apparent sample mass could be used to quantify the magnetic field strength. Figure 5a shows the T_c results at various changes of the apparent sample mass ranging from 0.27 to 15.6% by STA 8000. It indicates that T_c decreases firstly and increases slightly afterward with increasing change of the apparent sample mass. When the change of the apparent sample mass increases from 2 to 6%, T_c varies slightly. The T_c results at various changes of the apparent sample mass by Pyris 1 TGA shown in Fig. 5b have a trend similar with those by STA 8000.

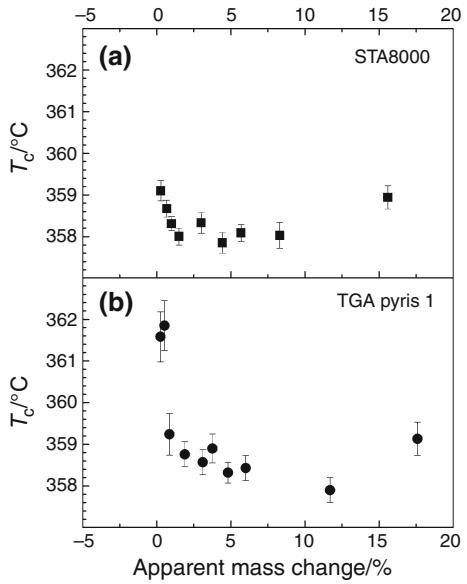

Fig. 5 T_c of nickel at varied change of the apparent sample mass by STA 8000 (**a**) and Pyris 1 TGA (**b**)

Garn et al. [4] regarded that the magnetic field strength has no obvious effect on T_c. Therefore, the collaborative study on GM 761 did not specify the magnetic field strength and only required that the change of the apparent sample mass should be big enough to observe Curie transition [4]. Gallagher and Gyorgy [8] demonstrated that T_c by TG is proportional to the cubic root of the magnetic field strength. Experimental results above showed that T_c by both STA and TG had a trend of decreasing firstly and increasing slightly afterward with increasing magnetic field strength (Fig. 5), which is quite different from that reported by Gallagher and Gyorgy [8]. Theoretically, the measured Curie point should increase with the magnetic field strength [8]. However, the initial decrease of T_c with increasing magnetic field strength is unexplained at present. Since T_c by both STA 8000 and Pyris 1 TGA was stable at around 5% of change of the apparent sample mass, it is specified that in the collaborative study the candidate of CRMs should be determined at around 5% of change of the apparent sample mass. It suggested that the temperature calibration of TG by CRM for T_c should be performed at the same change of apparent sample mass as that during the determination of CRM by STA for a better accuracy.

Effect of sample pan

The effect of the sample pan on T_c was investigated by using STA 8000. Figure 6a–c illustrates nickel and tin placed in the aluminum pan, the alumina pan with a flat bottom and the alumina pan with an arc bottom, respectively. The alumina pan with the arc bottom from PerkinElmer Co. is compatible with STA 8000.

Figure 7a–c shows T_m of metals and the modified T_c of ferromagnetic sample by STA 8000 using different sample pans. Since T_c of iron (771 °C) is higher than T_m of aluminum, it cannot be measured by using the aluminum pan. It indicated that T_m of the metals varied slightly with the type of sample pan (Fig. 7a–c). But T_c strongly depends upon the type of the sample pan. For example, T_c of nickel using the aluminum pan, the alumina pan with the plat bottom and the alumina pan with the arc bottom was 357.96, 357.68 and 359.29 °C, respectively. Namely, the difference of T_c resulted by the type of the sample pan could be as high as 1.33 °C.

Since the furnace of STA 8000 is vertical, the temperature of the surrounding is higher than that of the center, and thus, the heat flows from the surrounding to the center as shown in Fig. 6. A thin layer of 10 mg of nickel in the aluminum pan and the alumina pan with the flat bottom covered a large area (Fig. 6a, b). On the contrary, 1 mg of tin foil covered a small area in the center of pan (Fig. 6). The temperature of tin foil is close to that of the center of

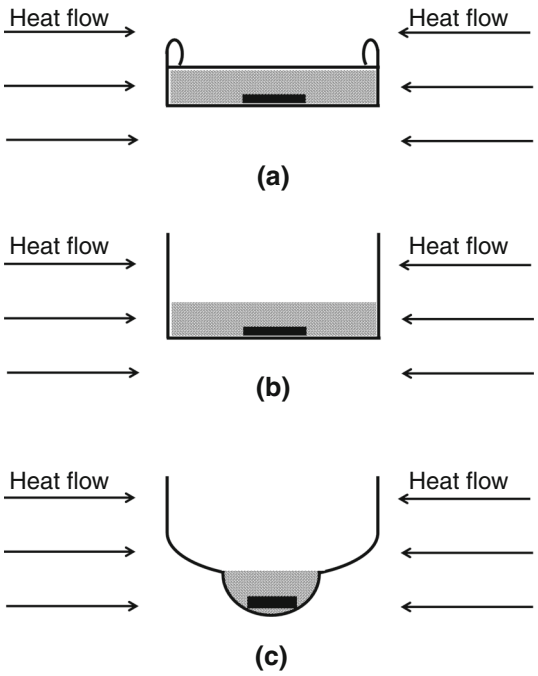

Fig. 6 Illustration of nickel and tin placed in different sample pans. *Grey*, nickel; *black*, tin. **a** Aluminum pan, **b** alumina pan with a flat bottom, **c** alumina pan with an arc bottom

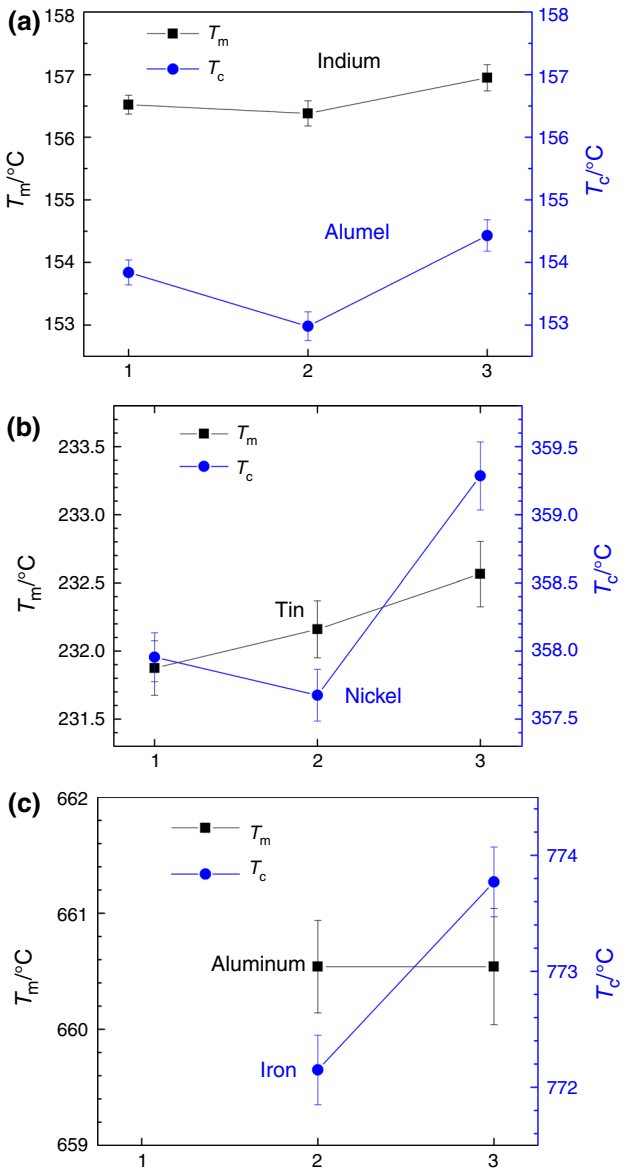

Fig. 7 T_m of indium and T_c of Alumel (**a**), T_m of tin and T_c of nickel (**b**), and T_m of aluminum and T_c of iron (**c**) by STA 8000 using different sample pans. *1* Aluminum pan. *2* Alumina pan with a flat bottom. *3* Alumina pan with an arc bottom

nickel thin layer and is less than that of the edge of nickel thin layer. The measured value of T_c represents the average temperature of all the parts of nickel thin layer during Curie transition. Therefore, T_c by using alumina pan with the flat bottom is the lowest (Fig. 7a–c). The temperature in the aluminum pan is more homogeneous due to the heat conductivity of aluminum. Therefore, T_c by using aluminum pan is the middle (Fig. 7a–c). The nickel powder in the alumina pan with an arc bottom concentrated in the center of pan as well as the tin foil, which makes the average temperature of nickel close to that of tin foil. Therefore, T_c by using the alumina pan with the arc bottom is the highest (Fig. 7a–c). In the collaborative study, the alumina pan with the arc bottom from PerkinElmer cannot be applied on STA from other manufacturers. Therefore, the collaborative study specified that Alumel and nickel were determined using the aluminum pan instead of the common alumina pan with the flat bottom for better accuracy, and iron had to be determined using the alumina pan with the flat bottom due to its melting point higher than aluminum. The effect of the type of sample pan on T_c might be different for the horizontal furnace of TGA/DSC1 and Q600.

Other effects on T_c including the mass of internal standard and the flow rate of the carrier gas of nitrogen were investigated. It demonstrated that the mass of internal standard has no obvious effect on T_c. And enough flow rate of nitrogen is necessary to prevent the oxidation of iron powder at high temperature. The collaborative study of T_c CRMs employed an optimized STA method including the fixed heating rate of 10 °C min^{-1}, the fixed change of the apparent sample mass of 5%, the mass of internal or external standard of 1 mg, and the mass of ferromagnetic sample of 10 mg. Alumel and nickel were certified by aluminum pan, and iron was certified by the alumina pan with the flat bottom.

Table 1 Results of T_c of three CRMs in the collaborative study

Lab no.	Alumel		Nickel		Iron	
	Means	SD	Means	SD	Means	SD
1	153.31	0.29	358.37	0.14	772.15	0.18
2	154.32	0.39	358.89	0.15	771.46	0.30
3	153.12	0.29	357.84	0.11	770.05	0.29
4	153.82	0.35	358.85	0.19	772.15	0.44
5	154.19	0.33	359.89	0.33	771.85	0.37
6	153.54	0.22	358.38	0.17	770.89	0.52
7	154.60	0.10	358.38	0.20	771.30	0.08
8	154.14	0.35	358.78	0.18	771.14	0.30
Means	153.9	–	358.7	–	771.4	–
SD	0.52	–	0.60	–	0.71	–

SD Standard deviation

Results of collaborative study

Eight laboratories took part in the collaborative study of T_c CRMs.[1] Two laboratories employed STA 8000, three laboratories employed TGA/DSC1, and three laboratories employed Q600. As shown in Table 1, the means of T_c of Alumel, nickel and iron are 153.88, 358.67 and 771.37 °C, respectively, with standard deviations of 0.52, 0.60 and 0.71 °C, respectively. These standard deviations (0.52–0.71 °C) are less than those of ICTAC-2 in the similar range of T_c (0.76–1.12 °C) [6]. The good repeatability of T_c by the collaborative study can be attributed to the modification of the STA method. The means of T_c were regarded as the certified value of CRMs for T_c.

Uncertainties

The uncertainty of the certified values was evaluated according to ISO guide 35 [9]. The uncertainty of T_c mainly comes from the dispersion of measurement results (type A uncertainty) and factors besides statistics (type B uncertainty). Type A uncertainty is evaluated using the standard deviation of the results of the collaborative study. Type B uncertainty includes the uncertainty from homogeneity, stability (long term and short term) and the certified method. The uncertainty from T_m of the internal or external standard is one component of type B uncertainty. It was so small that it can be negligible. The mass delay by the balance, the temperature difference between the internal or external standard and the ferromagnetic sample due to the temperature gradient might result the systematic errors of T_c. These systematic errors might vary with the instrument manufacturer. Therefore, uncertainties from these systematic errors were partly involved in the dispersity of certified results and then were ignored in the evaluation of type B uncertainty. Finally, the combined uncertainties of CRMs of Alumel, nickel and iron are 0.55, 0.63 and 0.75 °C, respectively. And the expanded uncertainties (U) of three CRMs are 1.1, 1.3 and 1.5 °C, respectively, with an expanded factor (k) of 2.

Calibration the temperature of TG needs a series of CRMs for T_c with a broad temperature range, such as from 100 to 1000 °C, and a suitable temperature interval, such as 150–200 °C [6]. Besides of three CRMs above, more CRMs for T_c is under development.

Conclusions

In this paper, CRMs of ferromagnetic, including Alumel, nickel and iron, for T_c were prepared and certified by the STA. The investigation demonstrated that T_c was affected by the heating rate, the magnetic field strength and the type of the sample pan. These CRMs were determined by the collaborative study using the optimized STA method with the fixed heating rate, change of the apparent sample mass and type of the sample pan. The certified values (the expanded uncertainties) of T_c of three CRMs are 153.9 °C (1.1 °C), 358.7 °C (1.3 °C) and 771.4 °C (1.5 °C), respectively. This series of CRMs for T_c can be used for the calibration of the temperature of TG with well accuracy.

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