High temperature calibration of DTA and DSC apparatus using encapsulated samples

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Abstract

A technique has been developed that permits metals with melting points in the range 1000–1500°C to be treated with hydrogen before encapsulation in quartz. The extrapolated onset temperature of melting of the metals was found to be linearly related to heating rates in the range 1–10°C per min. The value obtained by extrapolation to a zero heating rate was used as the melting temperature measured by the DTA instrument. A plot of this temperature against the published melting temperature gave a linear relationship with a correlation coefficient of 0.9999. Measurement of the peak areas allowed calculation of the cell correction factor, which again showed a linear relationship with temperature, with a correlation coefficient of 0.9303. These metals can thus be used to calibrate thermal analysis equipment for temperature and enthalpy in this temperature range. The samples showed no loss of integrity over many melting–freezing cycles.

Keywords: Calibration; DTA; Encapsulated standard; High-temperature thermal analysis; Hydrogen treatment; Quartz-encapsulation

1. Introduction

Thermal methods of analysis have become one of today's routine techniques for the characterisation of materials. The need for standard reference materials was recognised by McAdie [1] some 20 years ago, and in the intervening period various organisations, notably ICTA, have proposed materials and methods for the calibration of TA equipment for temperature and enthalpy.

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In the 1970s several papers [2–7] suggested the use of inorganic compounds, including double salts, as standard reference materials (SRMs). In 1984 Langier-Kuzniarowa [8] reported on six sets of NBS–ICTA certified SRMs for temperature calibration, resulting from the research work of the ICTA Standardisation Committee, with a highest calibration temperature of 940°C ($CaCO_3$). Further studies on eight of the recommended inorganic reference materials were made by Kostyrko et al. [9].

The International Temperature Scale of 1990 (ITS-90) reported refined melting points of many substances [10], but that list ended with the corrected copper melting point (1084.62°C) which was in the list of Secondary Reference Temperatures in The International Practical Temperature Scale of 1968 (IPTS-68) [11, 12]. The older list included the melting temperatures of nickel (1455°C) and cobalt (1495°C) as well. In 1990 Hohne et al. [13] presented a new recommendation for the correct temperature calibration of DSC and DTA instruments. In 1991 Dharwadkar et al. [14] used the method for high temperature calibration of DTA using the melting points of silver, copper, gold, nickel and cobalt as defining fixed points. This method needs a very large sample (500–600 mg) and very special arrangements such as high purity helium purge gas further purified by passing through molecular sieves, over hot calcium metal maintained at 550 K, and zirconium metal foil that was located close to the sample to act as a final oxygen scavenger. These special precautions are necessary to avoid oxidation of the metal samples. It is also impossible to use these pure metals with platinum crucibles due to their ability to form alloys with platinum [15].

Some papers were published in 1993 dealing with temperature calibration, but again limited to materials for calibration only up to 1100°C [15–18]. A literature survey on the subject quoting 88 references and covering the period between 1967 and 1991 has been published [19].

There has been an increasing trend for DTA and DSC equipment to be able to achieve temperatures of 1500°C or even 1600°C, and hence require calibrants in this temperature range. It seems that the best way for calibration between 1100 and 1600°C is by using the melting points of the elements from the IPTS-68 list, namely Cu, Ni and Co. The main problem with these elements is that they are easily oxidised and so sensitive to oxygen that even a small amount of oxide on the surface will change the peak shape and the onset temperature.

In this work a new method has been developed which enables the metals to be treated with hydrogen then encapsulated in a small fused silica bead. Such encapsulation prevents reaction between the metal sample and the surrounding atmosphere, enabling multiple use of the sample, without loss of integrity. The bead can also be contained in a sample crucible made of platinum or another metal.

2. Experimental

2.1. Sample preparation

High purity metal samples of at least 99.99% purity were obtained from Goodfellow Cambridge, UK. The sample was prepared by weighing 1–5 mg metal into 2.4/2.0 mm outer diameter/inner diameter fused silica tube joined to 2.4 mm diameter fused silica rod. The tube was connected to a vacuum system by a fused silica ground glass joint (see

Fig. 1). The system was evacuated to 1 mm Hg and filled with hydrogen. This process was repeated five times to ensure a pure hydrogen atmosphere in the system. The metal sample was heated to red heat, cooled, and the system evacuated to 1 mm Hg. The fused silica tube was sealed as close as possible to the sample, and the fused silica rod severed as close as possible to the bottom of the metal sample. The severed side of the sample was ground to achieve a smooth surface. The final shape of the encapsulation bead is shown in Fig. 1.

2.2. DTA measurement

All the work was performed with a Dupont 1090 Thermal Analyser with 1600DTA cell. Data analysis was carried out using the General Analysis utility program. The melting points of the encapsulated metals were measured in a platinum crucible with an empty one as a reference. Nitrogen gas flowing at $60 \, cm^3 \, min^{-1}$ was used unless otherwise noted. Before the DTA measurement was carried out the sample was heated to 30°C above the metal melting point to ensure good thermal contact between the metal and the base of the encapsulation bead. Every sample was measured for at least five heating rates, between 1 and 10°C min^{-1} and the exact heating rate was calculated afterwards using the time versus temperature curve.

3. Results and discussion

3.1. Preparation of samples

The sensitivity of the melting point to the hydrogen pretreatment is evident in Fig. 2, which shows the curves for the melting of copper. The first graph (Fig. 2A) is for the
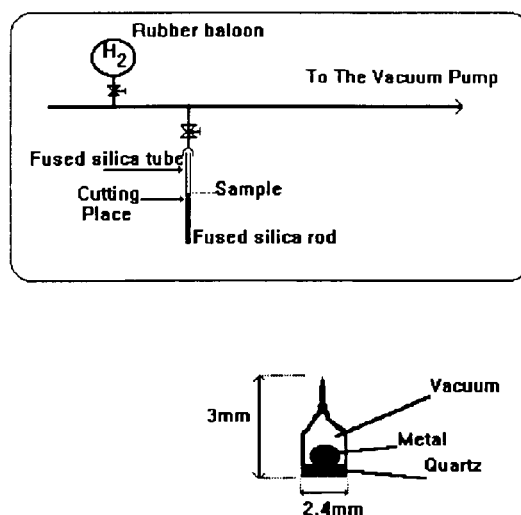

Fig. 1. Schematic diagram of the apparatus used for hydrogen treatment of metals prior to encapsulation in quartz.
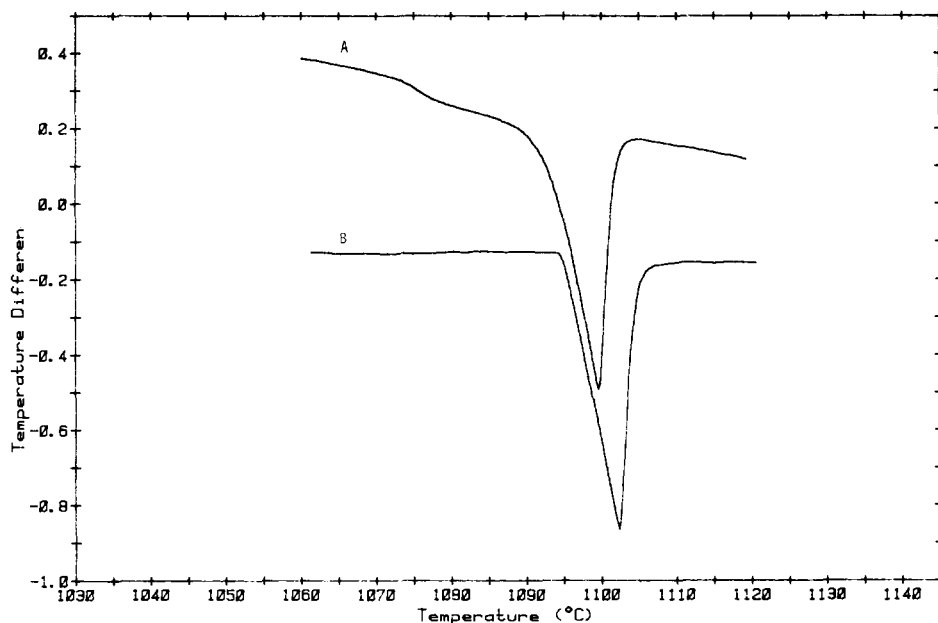
Fig. 2. DTA curves for copper encapsulated in quartz. Heating rate 10°C min^{-1}, platinum crucible. A, Goodfellow 99.999% purity as received; B, Goodfellow 99.999% purity after hydrogen treatment.

melting of the Goodfellow 99.999% copper, and the untreated material showed a deviation from the baseline commencing at 1074.5°C, with a major peak commencing at 1091.6°C. The hydrogen-treated material (Fig. 2B) has just a single peak with an onset temperature of 1095.3°C. Hence there are significant differences between the melting temperatures of the copper with and without hydrogen treatment.

3.2. Sensitivity of melting point determination to experimental parameters

Some experiments were performed to study the method sensitivity to experimental parameters. The parameter sensitivity study was performed with gold with and without the fused silica encapsulation process.

Fig. 3(a) shows the change of melting point of gold with increase of heating rate, with the encapsulated sample located centrally in a platinum sample pan and with a nitrogen flow rate of 60 cm^3 min^{-1}. The change of measured melting point with heating rate is very small, with a gradient of 0.0531. Hence these seem to be good conditions to use for the use of gold as a calibrant. Fig. 3(b) shows the same sample under the same conditions except that the nitrogen flow rate was reduced to 10 cm^3 min^{-1}. The gradient of the line of best fit is now 0.1697, which is more than three times the value of the line obtained at a flow rate of 60 cm^3 min^{-1}. However, the melting temperature value extrapolated to zero heating rate is only 0.3°C lower, so the flow rate effect is relatively minor. Fig. 3(c) shows the results for a bead which had been placed on the
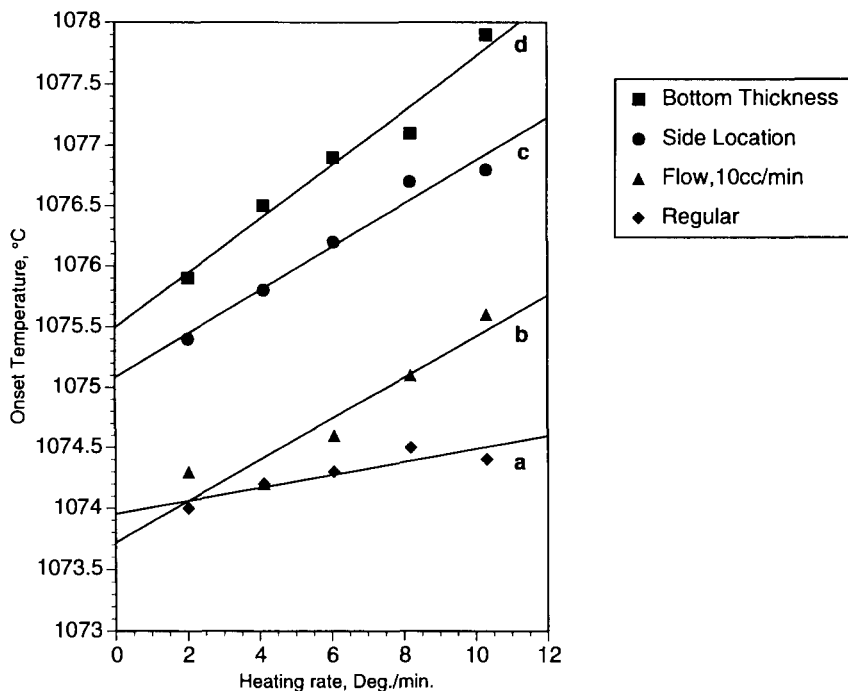
Fig. 3. Effect of experimental variables on the melting point measured by DTA of 99.99% purity gold encapsulated in quartz contained in a platinum crucible. (a) Effect of heating rate on the melting point of gold, nitrogen flow rate 60 cm³ min⁻¹; (b) as for (a), but with nitrogen flow rate of 10 cm³ min⁻¹; (c) as for (a), but with sample non-centrally located; (d) as for (a), but with a base thickness of twice the value used for the other encapsulating beads.

edge of the pan, so that the sample was not centrally located. The gradient of the line is similar to that for Fig. 3(b), but has been displaced by approximately 1.1°C to a higher value. Hence careful location of the sample is essential for reproducible results. The final set of results shown in Fig. 3(d) is for a glass encapsulating bead which has a base which is approximately twice as thick as for the other samples. This was achieved by less grinding of the base. The gradient of the line is steeper than for any of the other curves, and so for the higher heating rates, for example 10°C min⁻¹, the difference in temperature between 3(a) and 3(d) is 4°. However, at zero heating rate the difference is 1.5°. The difference between the results for 3(d) and the others is caused by an increase in the thermal lag of the sample as the base thickness is increased.

3.3. Reproducibility studies

Reproducibility tests were performed by making several of the quartz encapsulated beads for each metal and determining the onset temperature of melting, with due consideration of the factors set out above. The results obtained are given in Table 1.

Table 1
Reproducibility of the melting points of different encapsulated samples of specific metals

Metal	Sample no.	Mean melting temperature/ °C
Silver	1	974.2
	2	971.3
	3	972.4
Gold	1	1074.6
	2	1075.4
	3	1075.3
	4	1073.4
	4*	1072.8
Copper	1	1092.7
	2	1095.6
	3	1095.1
Silicon	1	1433.5
	2	1433.4
	3	1432.7
Nickel	1	1479.6
	2	1479.9
	3	1479.8

* see text

Each bead was placed in the DTA cell and cycled at least four times at a heating rate of $10°C\,min^{-1}$ across the melting endotherm, and the mean melting point temperature calculated. The bead was then taken out and a new one introduced and the process repeated. One sample caused difficulties. The melting point of cobalt was the closest of the group to the melting point of quartz. After two or three cycles, the melting temperature was observed to shift, and on inspection of the quartz bead it was found that cracks had developed in the structure permitting the ingress of air. Some beads lasted for six or seven cycles, but beads heated to these kinds of temperatures, that is above 1500°C, were clearly not as robust as those heated to lower temperatures.

Although the reproducibility for a specific sample has a low associated standard deviation, of between 0.1 and 0.3, there was up to a 3°C difference in melting point value between experiments on different beads containing the same metal. Some of this lack of reproducibility could be attributed to the differences in the structure of the bead, as well as a contribution from the placement of the bead in the sample crucible. The DTA head used in these experiments had a rounded base, and hence it was not always easy to site the bead in a reproducible manner. We are currently doing a similar study on a flat plate DTA system which makes bead placement rather simpler.

All of the tests reported in Table 1 were carried out with the bead in a platinum crucible. One experiment was carried out with Sample 4 containing gold placed in an alumina sample crucible (see * result). The average melting temperature for five cycles was found to be 1072.8°C, which compared well with the value of 1073.4°C found for the bead in a platinum crucible. Another experiment was conducted with unencap-

sulated gold in an alumina pan, and the melting temperature found to be 1071.0°C, 1.8°C lower than the encapsulated sample.

3.4. Melting point measurements

The extrapolated peak onset temperature versus the heating rate for Ag, Au, Cu, Si, Ni and Co are shown in Figs. 4 to 9, respectively. All the samples except Au and Si had
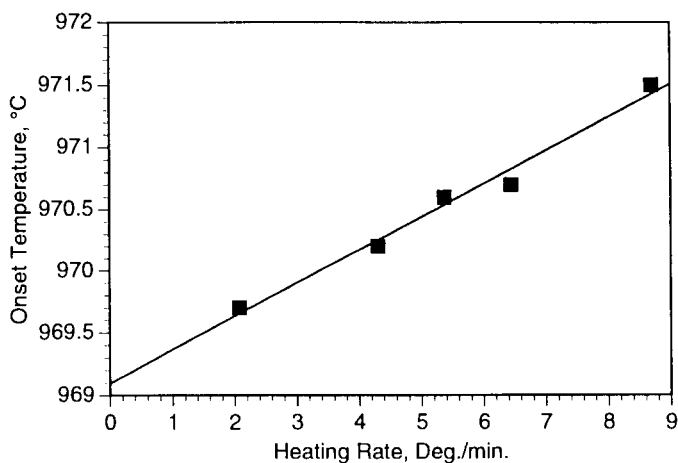

Fig. 4. Plot of extrapolated onset temperature of melting against heating rate for silver (99.99% purity). Correlation coefficient 0.9832.
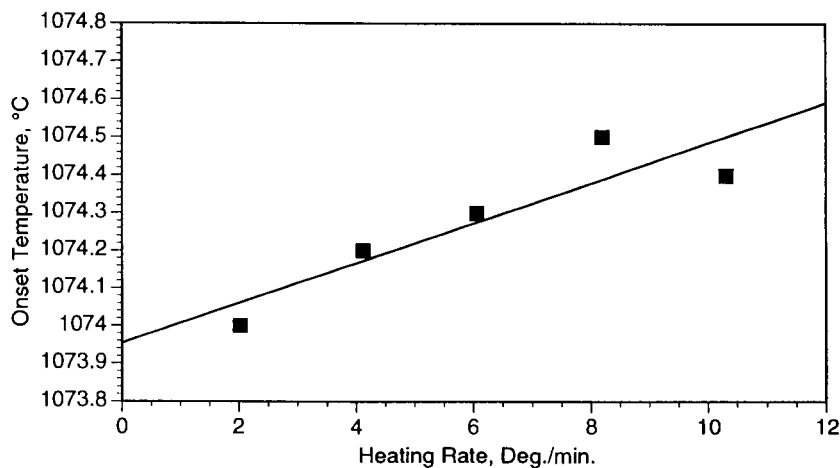

Fig. 5. Plot of extrapolated onset temperature of melting against heating rate for gold (99.99% purity). Correlation coefficient 0.8132.
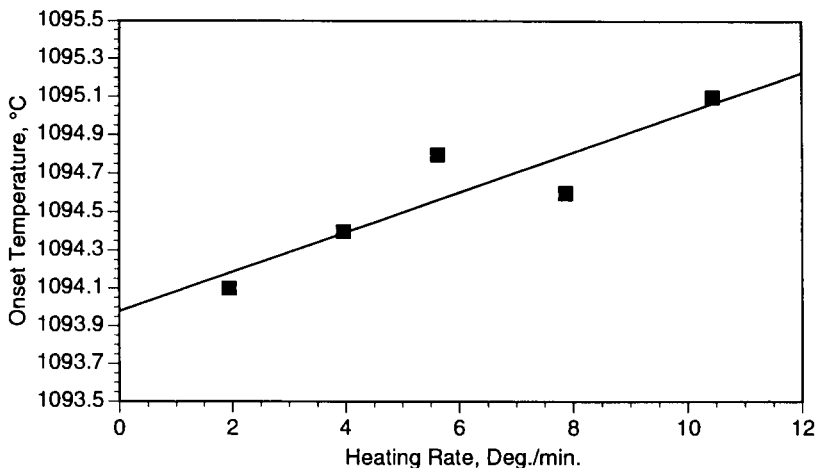
Fig. 6. Plot of extrapolated onset temperature of melting against heating rate for copper (99.999% purity). Correlation coefficient 0.8230.
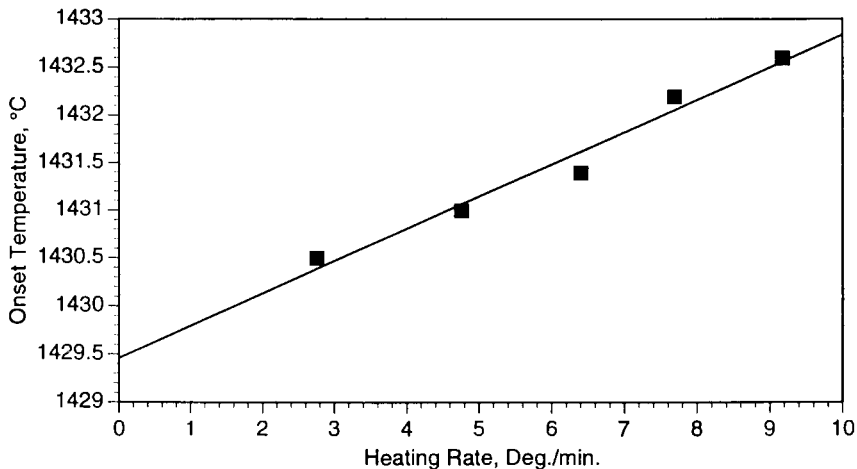

Fig. 7. Plot of extrapolated onset temperature of melting against heating rate for silicon (99.999% purity). Correlation coefficient 0.9700.

been treated with hydrogen before encapsulation in fused silica. The melting points of Au and Si were found to be single well defined peaks and so it was considered not necessary for them to be treated with hydrogen. The extrapolated peak onset temperatures for the melting points of the metals at zero heating rate were determined from the graphs, and used as the melting point temperatures indicated by the measuring
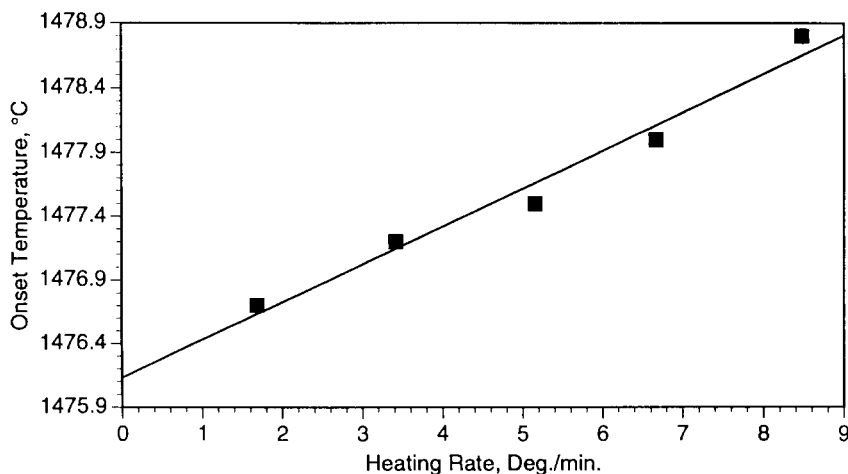
Fig. 8. Plot of extrapolated onset temperature of melting against heating rate for nickel (99.999% purity). Correlation coefficient 0.9730.
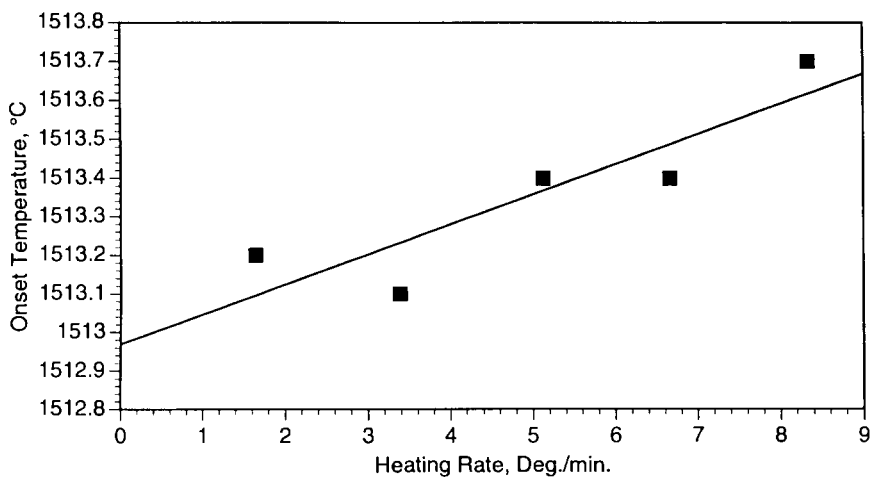

Fig. 9. Plot of extrapolated onset temperature of melting against heating rate for cobalt (99.99% purity). Correlation coefficient 0.7939.

instrument. A summary of the results is shown in Table 2, and a plot of the known melting points versus the temperature correction needed for the instrument is shown in Fig. 10.

3.5. Fusion enthalpy

The fusion enthalpies of the recommended elements, and the average peak area of at least five measurements at different heating rates, are shown in Table 3. It is well known

Table 2
Melting points of the elements compared to those measured by differential thermal analysis

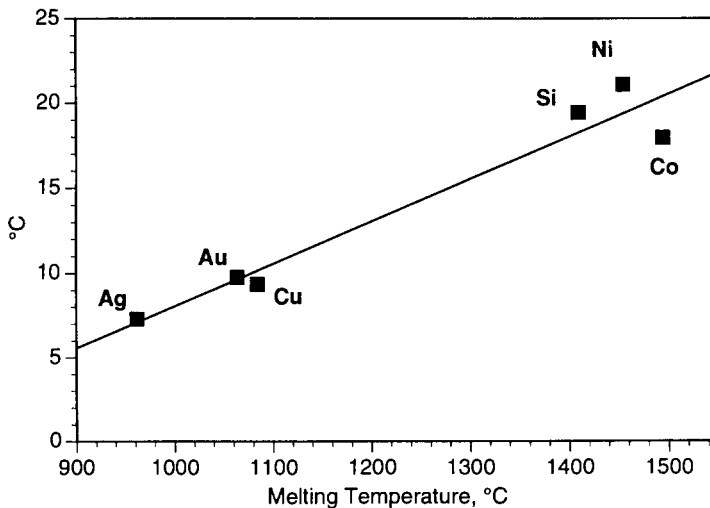| Element	Melting point as indicated by the instrument/°C	Melting point as known [11]/°C	Temperature correction needed/°C
Ag	969.1	961.8	7.3
Au	1073.9	1064.2	9.7
Cu	1094.0	1084.6	9.4
Si	1429.5	1410	19.5
Ni	1476.1	1455	21.1
Co	1513.0	1495	18.0

Fig. 10. Difference between recorded melting temperature determined by DTA and literature value, as a function of temperature.

that the response of DTA equipment varies with temperature. To assess this for the temperature range 1000–1500°C, the peak area for the melting transition was divided by the enthalpy of melting for each of the metals. This provided a cell correction factor

$$F = P_a/H_f$$

where: F is the cell constant (or cell correction factor), J deg^{-1} min^{-1}; H_f, is the fusion enthalpy J g^{-1}; and P_a is the average peak area, deg min g^{-1}.

A plot of the cell correction factor versus temperature is shown in Fig. 11. It can be seen that there is a linear correlation between temperature and the correction factor, and that the instrument response diminishes as the temperature increases. From

Table 3
Calculated cell constant values as a function of temperature

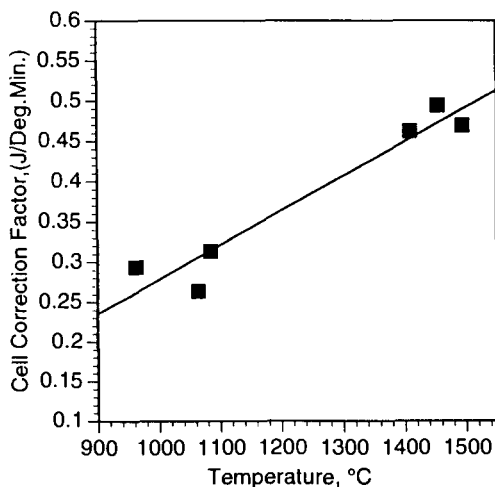| Element	Transition temperature/°C	Fusion enthalpy/(J g^{-1})	Peak area/ (deg min g^{-1})	Cell constant/ (J deg^{-1} min.$^{-1}$)
Ag	961.8	10.47	35.7	0.293
Au	1064.2	6.45	24.46	0.264
Cu	1084.6	20.47	65.38	0.313
Si	1410	140.92	304.6	0.463
Ni	1455	29.98	60.68	0.494
Co	1495	25.81	54.96	0.470

Fig. 11. DTA cell correction factor as a function of temperature. Correlation coefficient 0.9303.

961–1495°C the instrument sensitivity decreases by almost half. Consequently it is necessary to calibrate the DTA for enthalpy in the temperature range of interest, a not unexpected finding.

4. Conclusions

The hydrogen treatment and encapsulation technique is a relatively simple method for the production of metal samples with a single sharp melting endotherm which can be used to calibrate DTA or DSC apparatus for temperature and enthalpy in the temperature range 1000–1500°C. There was some variation in the measured melting temperatures with change in experimental conditions, but the effect was small when the melting temperatures were extrapolated to a zero heating rate. Nevertheless the changes that occurred in the measured values with change in experimental conditions

emphasise the need for careful standardisation of procedures to give reproducible results. The encapsulation prevents oxidation of the metal, and no special precautions are required to exclude air or oxygen from the equipment. With the exception of the cobalt sample, the samples can be used for many repeat experiments.

The method fulfilled all the general requirements for calibration substances [15], but still needs to be assessed for more experimental parameters before being submitted for a round-robin test to ensure the exact reproducibility and accuracy of the method.

Acknowledgements

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