

Reference Materials for Calibration of Temperatures in DTA/DSC Instruments

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ABSTRACT

This report details the work carried out to produce two reference materials for the temperature calibration of high temperature DSC and DTA instruments. Several potential reference materials were tested, two are recommended for calibration purposes, viz

- (i) pure iron, using the $\gamma \rightarrow \delta$ transition at 1392 °C and
- (ii) 40% Ni - 60% Pd using the minimum of solidus and liquidus temperature of 1237 °C.

The onset temperature was found to give reliable values for the solidus temperature and it is recommended that very small specimens should be used for measurements of peak temperatures.

This investigation has revealed that oxygen ingress can have a significant effect on temperature calibrations. In order to minimise oxygen ingress in the DTA/DSC it is recommended that:

- (i) all plastic tubing in the DSC and the gas train should be replaced with stainless steel tubing and fittings and that these should be checked to ensure that the train is gas-tight and free from moisture;
- (ii) the furnace tubes should be frequently examined to detect cracks in the tubes;
- (iii) frequent checks with the reference materials should be carried out and measurements with the δ -iron may be particularly useful and
- (iv) oxygen probes should be fitted to the exit lines of the gas train to detect oxygen ingress.

The results obtained with the Fe-Pd and Co-Pd alloys (used as potential reference materials) were not consistent with the published phase diagrams.

An interlaboratory comparison project involving 4 laboratories was carried out and this showed that both the materials were suitable for calibrating the temperature scales of DSC instruments.

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head, Centre for Materials Measurement and Technology

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1 BACKGROUND

Differential thermal analysis (DTA) is a popular technique for determining temperatures of transitions and DTA instruments can be found in many laboratories. Developments in recent years has led to quantitative DTA which is often referred to as differential scanning calorimetry (DSC). It has recently been shown that DSC can be used to determine heat capacities and enthalpies of alloys up to 1500 °C [1]. However, this study [1] revealed the absence of a reference material to calibrate the temperature scales of DTA and DSC instruments in the temperature range between the melting points of Cu and Ni (1085 to 1450 °C).

A satisfactory reference material should have the following features:

- (i) it should melt at a discrete temperature;
- (ii) it should be stable and inert to reactions with the container materials and the gaseous atmosphere (eg Si has a melting point of 1414 °C but would be an unsatisfactory reference material since its affinity for oxygen causes the sample to react with both alumina and the gas environment);
- (iii) for alloy systems it would be desirable to have eutectic melting temperatures which are insensitive to chemical composition to ensure that any departures from the target compositions would have little effect on the eutectic temperature.

The objective of this study was to produce two satisfactory reference materials for the calibration of the temperatures in the range 1100 to 1450 °C.

2 SCIENTIFIC PROGRESS

2.1 IDENTIFICATION OF POTENTIAL REFERENCE MATERIALS

The phase equilibria for a large number of pure metals and binary alloys were scrutinised to identify potential reference materials with transitions in the range between 1085 °C and 1450 °C. Four potential transitions were identified:

- (i) γ (austenite) $\rightarrow$ δ Fe transition reported to occur at 1394 °C [2];
- (ii) Fe-Pd with a “minimum” temperature of 1310 °C (Figure 1) [3];
- (iii) Ni-Pd with a “minimum” temperature of 1237 °C (Figure 2) [3] and
- (iv) Co-Pd with a “minimum” temperature of 1217 °C (Figure 3) [3].

Inspections of Figures 1 to 3 indicate that the minimum in the solidus and liquidus temperature curves are very flat with respect to composition and that all three systems would be tolerant to deviations from target compositions.

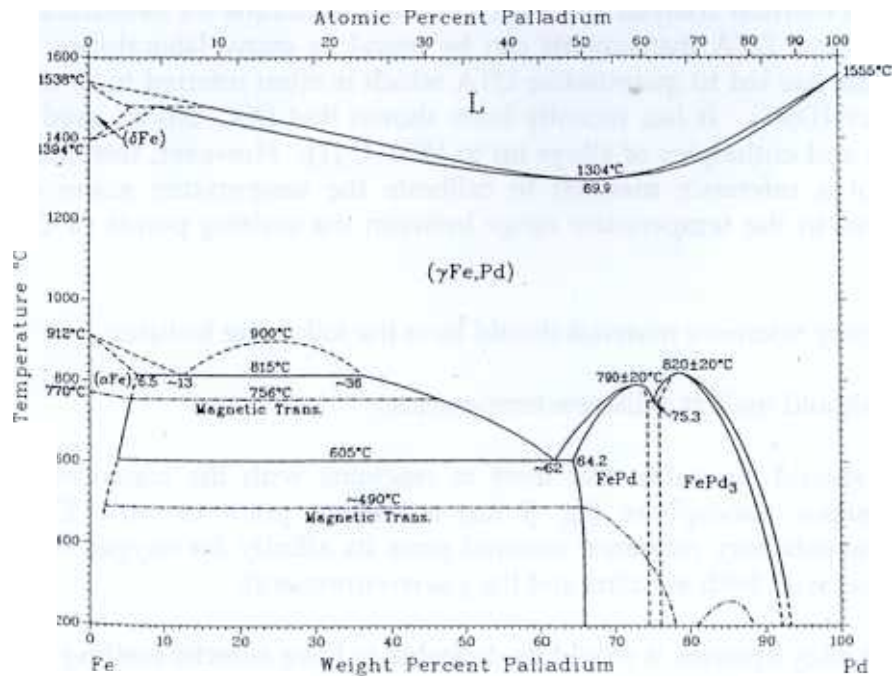


Figure 1 Phase diagram of Fe-Pd system [3].

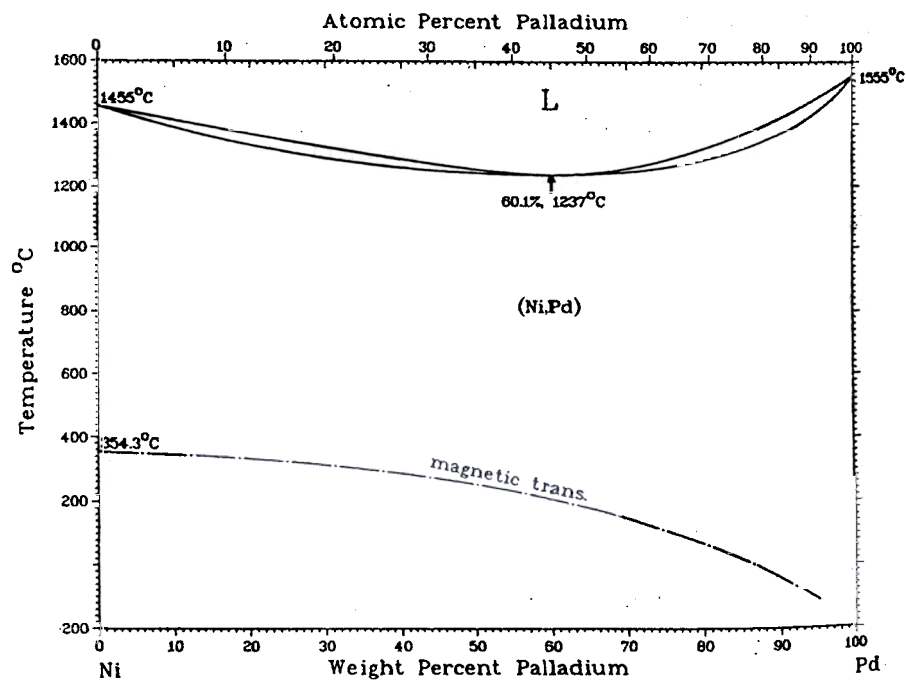


Figure 2 Phase diagram for the Ni-Pd system [3].

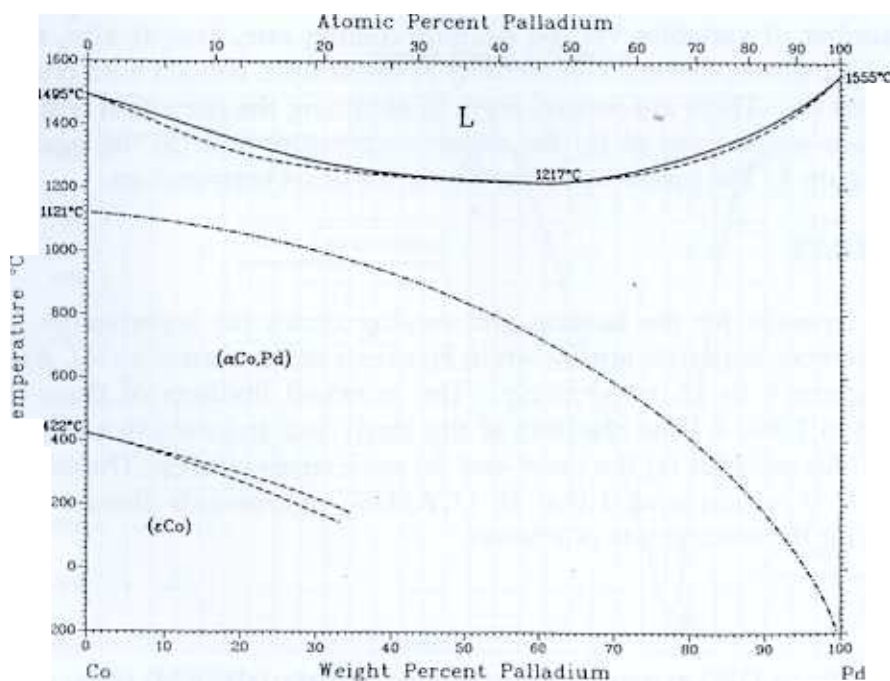


Figure 3 Phase diagram for the Co-Pd system [3].

2.2 EXPERIMENTAL

Reference Materials

The iron sample used in this investigation was specpure grade supplied by Johnson-Matthey with a reported purity of 99.9985%.

The samples of Fe-Pd, Ni-Pd and Co-Pd were prepared from metals Fe (99.9985%), Ni (99.9%), Co (99.9%) and Pd (99.9%). They were prepared from weighed amounts of the pure metals and were melted for 1 minute using cold crucible levitation (to avoid contact with oxide materials) in an argon atmosphere. The target compositions are shown below.

Target composition: 38.5% Co + 61.5% Pd
 30.0% Fe + 70% Pd
 40% Ni + 60% Pd

Apparatus and Procedure

The DSC experiments were carried out in a Stanton-Redcroft DSC 1500. The samples were placed on alumina discs held in platinum crucibles fitted with platinum lids. The experiments were carried out using a flowing atmosphere of argon and using heating and cooling rates of 10 Kmin⁻¹. Further details of the method have been given elsewhere [1].

When a sample undergoes an endothermic (or exothermic) transition, heat is absorbed (or evolved) by the sample. DTA/DSC is a dynamic method and time is required to absorb (or

When a sample undergoes an endothermic (or exothermic) transition, heat is absorbed (or evolved) by the sample. DTA/DSC is a dynamic method and time is required to absorb (or evolve) this heat. The net result is that the DSC trace exhibits a peak, similar to that shown in Figure 4 but there is some lag in the response. This temperature lag will be dependent upon a number of variables viz the heating/cooling rate, sample size, magnitude of the enthalpy of transition, thermal conductivity of the sample, contact with crucible, presence of alumina discs etc. There are several ways of obtaining the transition temperature; the two most common are the use of (a) the onset temperature and (b) the peak temperature as shown in Figure 4. The present authors favour the onset temperature.

2.3 RESULTS

Typical DSC results for the heating and cooling cycles for experiments run on the four potential reference materials are shown in Figures 5 to 8 and runs on Al, Au, Cu and Ni are given in Figures 9 to 12, respectively. The principal findings of these experiments are summarised in Table 1. The objective of this study was to establish a reliable correction to the temperature scale for (a) the onset and (b) peak temperatures. The results are shown in Figure 13. It is recommended that all DTA/DSC instruments should be calibrated in a similar way for the heating rate of interest.

Table 1
Results of DSC experiments on reference materials (RM) for experiments
carried out for a heating rate of 10 Kmin⁻¹

RM (mass, mg)	T _{trans} °C (literature)	T _{meas} °C		(T _{meas} - T _{lit})		Comments
		Onset	Peak	Onset	Peak	
Al (36-51)	660.5	658 ± 1.4 ^(a)	682 ± 4.7	-2.5	+21.5	Oxide film could affect heat transfer
Au (27-339)	1064.5	1060 ± 1.9 ^(a)	1075 ± 4.2	-4.4	+10.6	Tended to 'ball up', only first heating run can be used
Cu (40-279)	1084.9	1062 ± 0.7 ^(a)	1087 ± 9.3	-22.9	+2.1	Small double peak possibly eutectic with Cu ₂ O (1065 °C)
Ni (42-256)	1455	1436 ± 1.6 ^(a)	1454 ± 8.6	-19	-1	Small double peak possibly (NiO 1438 °C)
δ-Fe (38-294)	1392	1388 ± 2.2 ^(a)	1391 ± 3.2	-4	-1	Two peaks, one attributed to oxide formation
Fe-Pd (16-191)	1310	1312 ± 21 ^(a)	1337 ± 7.5	+2	+27	
Ni-Pd (47-196)	1237	1228 ± 7 ^(a)	1246 ± 3	-9	+9	
Co-Pd (15-36)	1217	1253 ± 1.0 ^(a)	1264 ± 0.8	+36	+47	

(a) ±value represents standard deviation (95%).

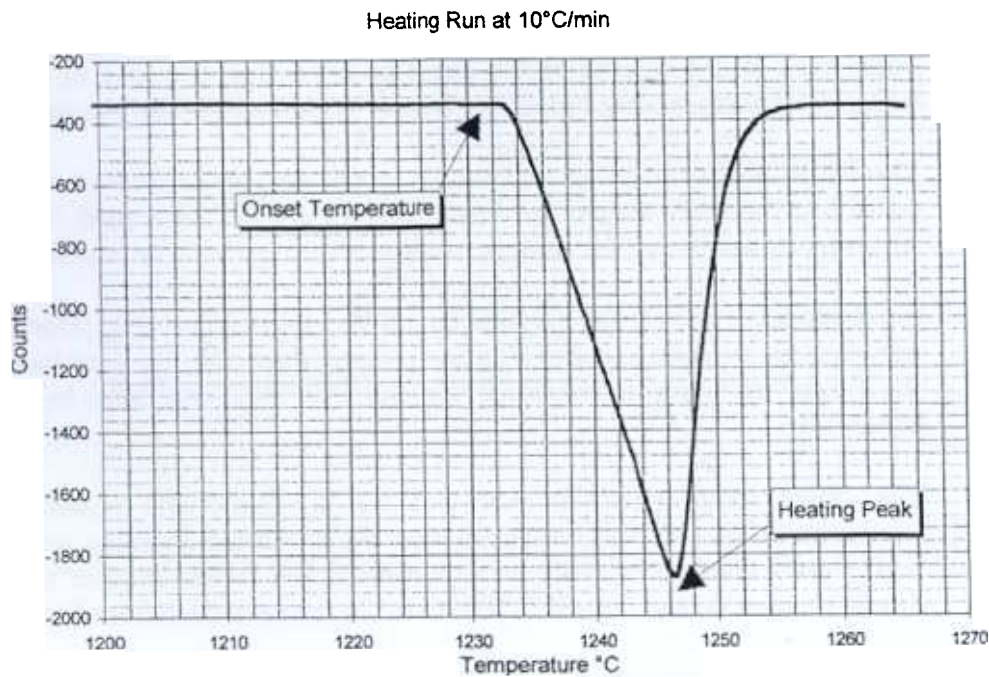


Figure 4 Schematic diagram showing the onset and peak temperatures during the heating cycle.

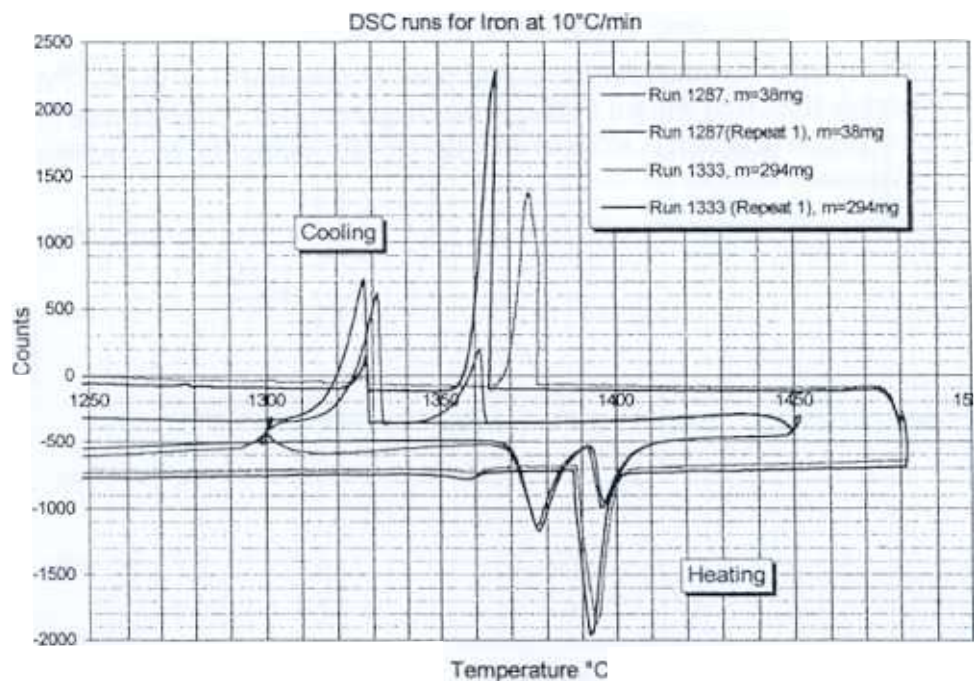


Figure 5 DSC traces for pure Fe in the environment of the γ - δ transition with heating and cooling rates of 10 Kmin⁻¹.

Inspection of Figures 5-12 and Table 1 indicate the following:

- (i) Supercooling of the metal occurs during the cooling cycle and consequently measurements for the cooling cycle cannot be used for calibration of the temperature scale. The Ni-Pd showed only a small undercooling and may be worth considering as a calibrant on cooling especially if a very small specimen was used.
- (ii) The onset temperature for Al was in good agreement with the accepted melting point but the peak temperature provided a poor measurement; it is suggested that this may be related to the oxide formation affecting the heat transfer.
- (iii) Gold tended to 'ball up' on melting on the sapphire giving poor thermal contact between the sample and the alumina plaque; thus only the first heating run can be used and the peak temperature for the first run may also be affected by this behaviour.
- (iv) The onset temperature for Cu was 20 °C below the recommended melting temperature, this strongly suggests that the specimen contains contaminants; since high purity Cu was used in the experiments the contamination is almost certainly due to oxygen (ie air) ingress (0.39% O in Cu causes a decrease of 18 °C in the mp).
- (v) The onset temperature for Ni provided a poor measurement of the melting temperature which again suggests that the nickel had been contaminated with oxygen (0.24% O in Ni causes a decreases of 15 °C in the mp of Ni).
- (vi) These were two peaks observed in the DTA traces following the $\gamma \rightarrow \delta$ Fe transition (Figure 5), one at 1363 °C was attributed to the melting of FeO (1373 °C) and the second peak to the ($\gamma \rightarrow \delta$) transition; the onset and peak values both provided reasonable measurements.
- (vii) The results obtained for onset and peak temperatures of the Co-Pd sample are much higher than that shown in the phase diagram (1217 °C see Figure 3) this suggests that the phase diagram is in error and the Co+Pd cannot be recommended as a reference material.

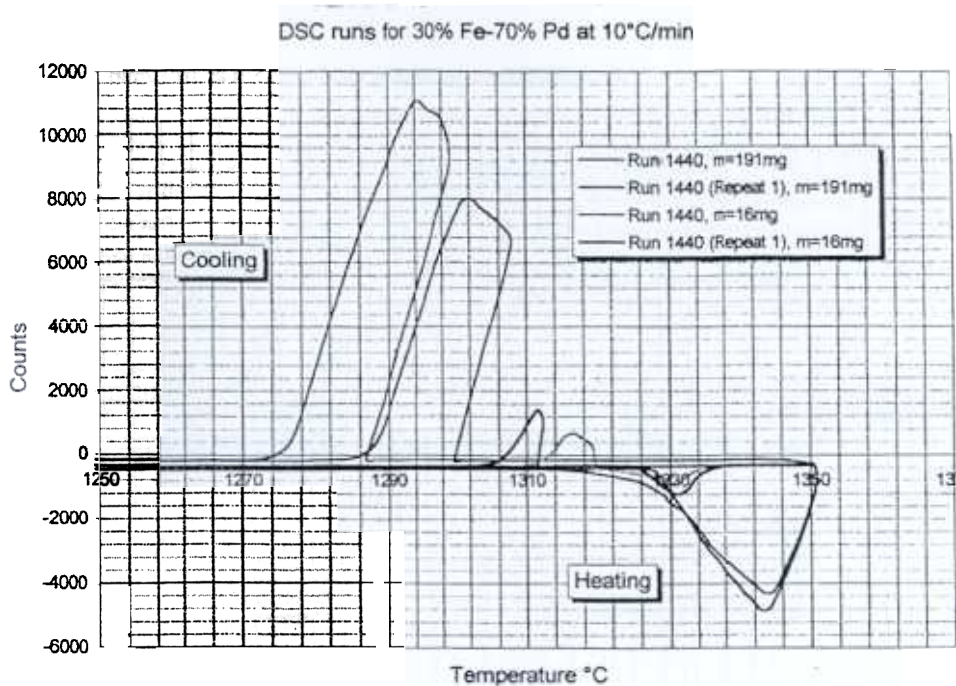


Figure 6 DSC traces for 30% Fe + 70% Pd for heating and cooling rates of 10 Kmin⁻¹.

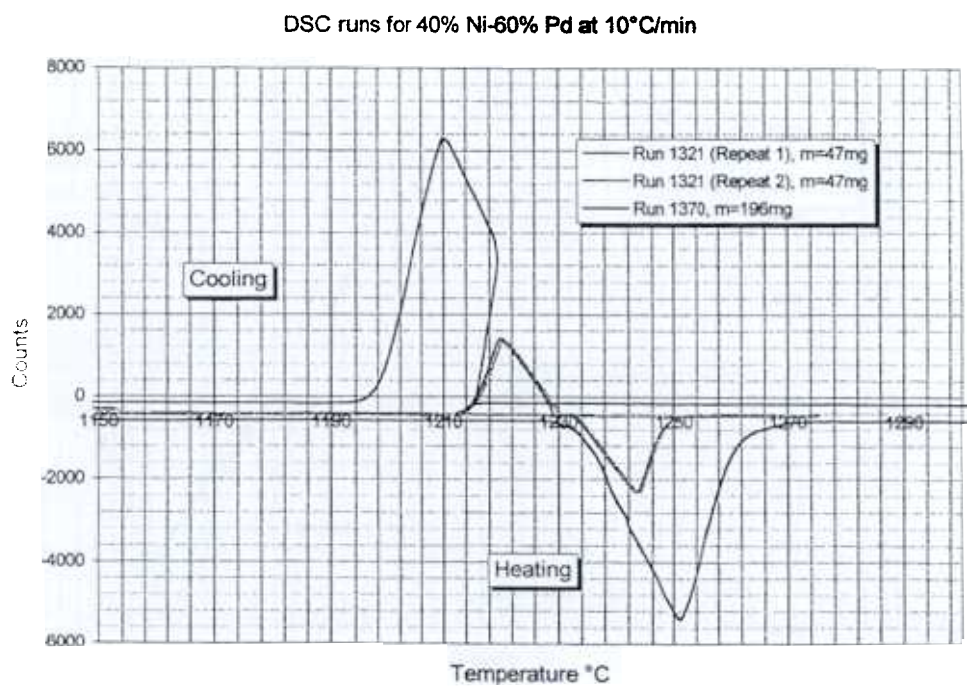


Figure 7 DSC traces for 40% Ni + 60% Pd for heating and cooling rates of 10 Kmin⁻¹

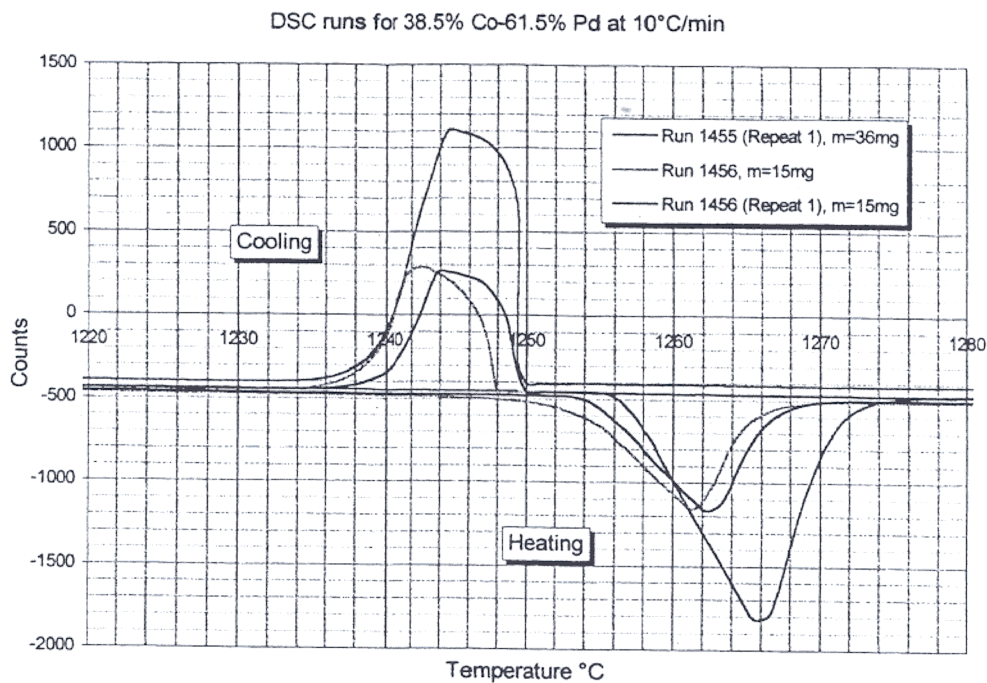


Figure 8 DSC traces for 38.5% Co + 61.5% Pd for heating and cooling rates of 10 Kmin⁻¹.

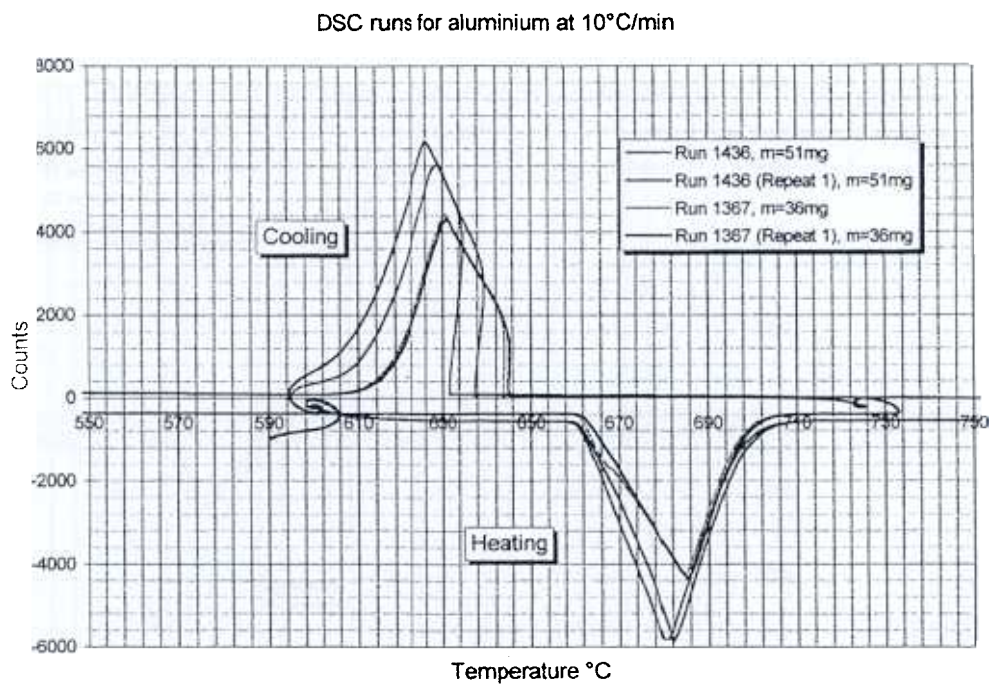


Figure 9 DSC traces for pure Al using heating and cooling rates of 10 Kmin⁻¹

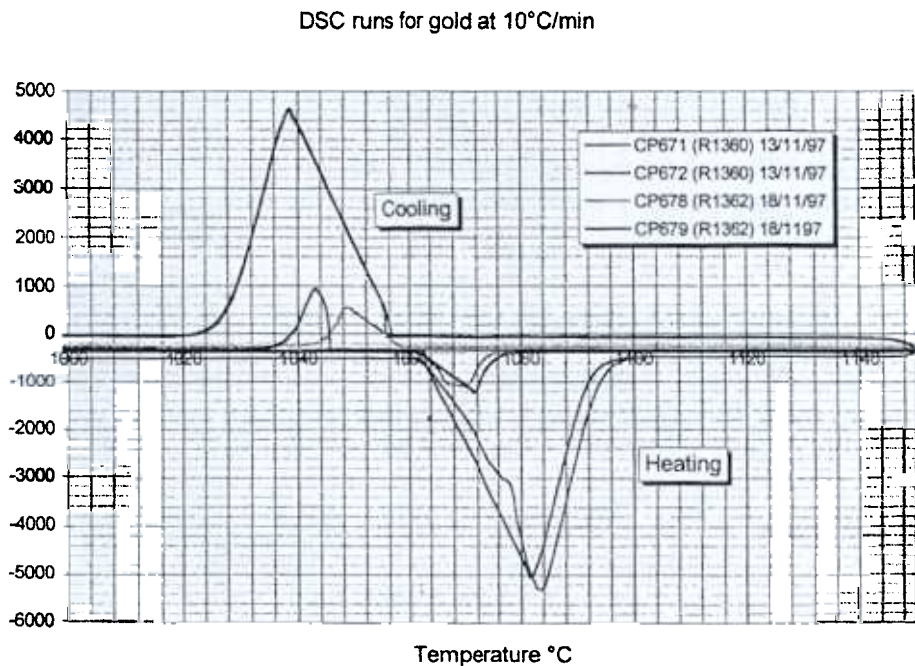


Figure 10 DSC traces for pure Au using heating and cooling rates of 10 Kmin⁻¹

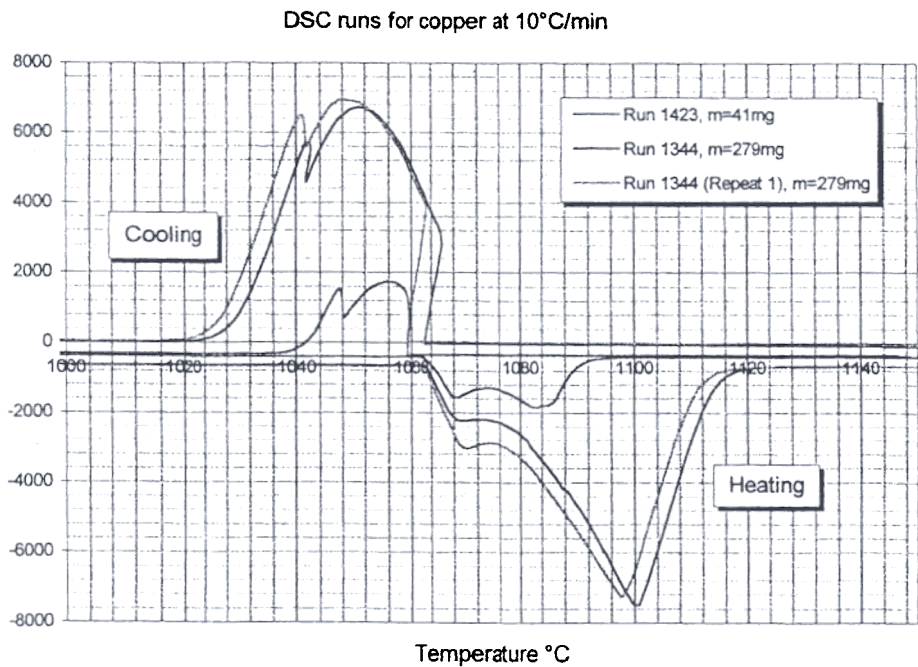


Figure 11 DSC traces for pure Cu using heating and cooling rates of 10 Kmin⁻¹

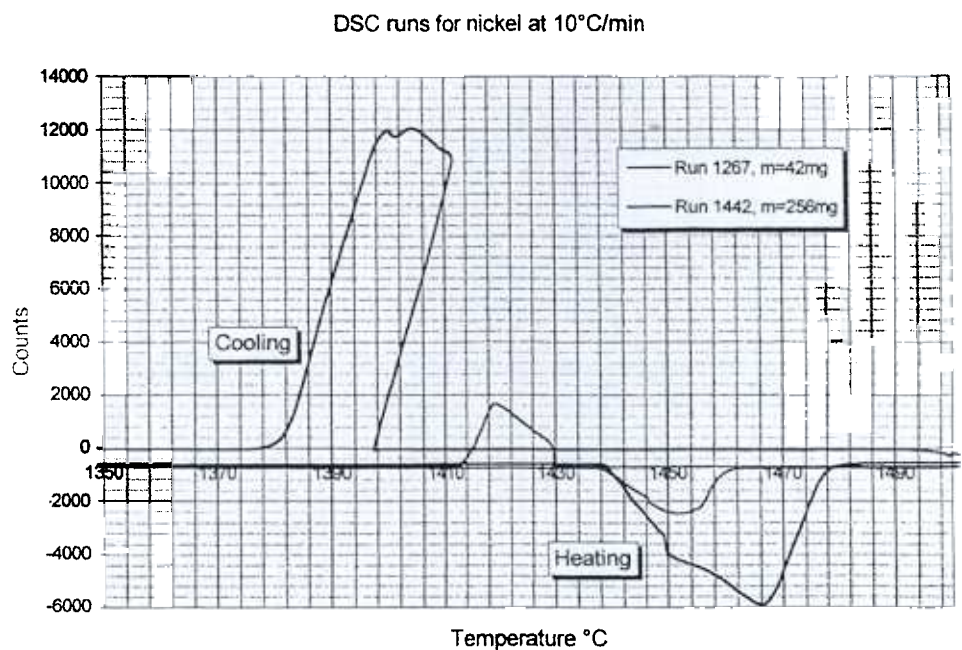


Figure 12 DSC traces for pure Ni using heating and cooling rates of 10 Kmin⁻¹

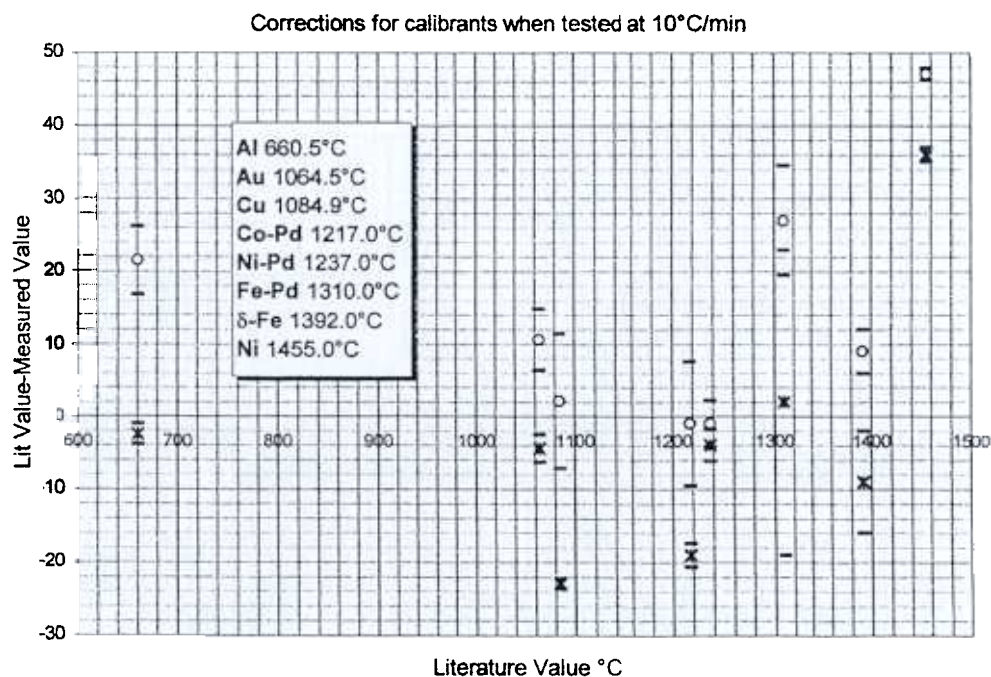


Figure 13 Corrections ($T_{\text{meas}} - T_{\text{lit}}$) for onset and peak temperatures for various calibrants as a function of temperatures when using a heating rate of 10 Kmin⁻¹; X, onset temperature; O, peak temperature.

- (viii) The Fe-Pd results show that the onset temperature provides a reasonable measurement of the “minimum” temperature but the correction for the peak temperature would have to be much higher than those involving the melting process for other metals (eg Au, Ni-Pd); one possible reason is the existence of a (solid + liquid) region spanning a 10 °C interval.
- (ix) The Ni-Pd results for onset and peak temperatures provide reasonable measures of the “minimum” temperatures and thus constitutes a useful reference material for temperature calibrations.

2.4 DISCUSSION OF RESULTS

The use of the onset temperature as a way of calibrating the temperature scale is sound providing the sample has not been contaminated, if it is contaminated it would be prone to some premelting. However, when applied to commercial alloys with a distinct melting range, the onset temperature can only be used for the determination of the solidus temperature. In these cases the liquidus temperature can only be determined from the peak temperature. Thus it is important to have corrections for both onset and peak temperatures. The peak temperature corrections could be affected by a series of factors (i) sample mass; (ii) magnitude of enthalpy of fusion; (iii) the heat transfer resistance between sample and thermocouple, so they are prone to a larger and more variable correction term. Nevertheless, peak temperatures are important since they provide the route to obtaining the liquidus temperature.

It is apparent from this investigation that ingress of oxygen from air can have a significant effect on the results obtained for the melting range. The ingress of oxygen can come from several sources:

- (i) cracks in the furnace tube;
- (ii) leakage into the gas line.

Furnace tube cracking was quite a frequent experience in this study and it is recommended that frequent examination should be carried out to detect cracking. Leaks in the line are particularly difficult to avoid. It is recommended that for all high temperature DSC measurements plastic tubing in gas lines should be replaced with stainless steel tubing and fittings but even here great care must be taken to ensure that the fittings are gas-tight and that the lines are free from moisture. Thus frequent checks should be carried out with the reference materials. The insertion of an electrochemical cell to measure oxygen in the gas flow leaving the furnace would also be useful of detecting oxygen ingress. This investigation has been most useful in highlighting the dangers of oxygen ingress on the results. However, these problems will possibly be less important in commercial alloys which frequently contain elements like Al which restrict the solubility of oxygen but the oxide films produced may pose other problems.

It is apparent that the ($\gamma \rightarrow \delta$) transition at 1392 °C provides a very useful reference material for calibration of the temperature scale. The Ni-Pd alloy is also recommended as a reference material but the work carried out here suggests that the reported phase diagrams for the Co-Pd, and more especially, Fe-Pd alloys, may be in error.

3 INTERLABORATORY COMPARISON

Since the Ni-Pd and γ - δ Fe transition appeared to be useful reference materials for temperatures calibration. An interlaboratory comparison was established to test the calibrant. Four laboratories, National Physical Laboratory, Netzsch, Nottingham University and Federal Mogul (formerly T&N) participated in the “round robin” project. Details of the instruments and the experimental conditions used by the four participating laboratories are shown in Table 2. The results obtained for the 40% Ni-60% Pd alloy are given in Table 2 and Figure 15 and those for γ - δ Fe transition are given in Table 13 and Figure 14. The onset temperatures were determined on the heating and cooling cycles.

It can be seen that from the results given in Tables 2 and 3 that

- (i) the proposed reference materials are suitable for the calibration of temperature;
- (ii) the onset temperatures for $\gamma \rightarrow \delta$ Fe transition and Ni-Pd melting were in good agreement, with the exception of the values recorded by Laboratory B on the heating cycle; these results suggest that the temperature scale of the DSC in Laboratory B needs to be calibrated;
- (iii) the use of a very small sample adopted by Laboratory D resulted in onset temperatures which were (a) very close to the recommended values and (b) very similar for both heating and cooling cycles (ie little undercooling).

Table 2
**Measurement of Solidus and Liquidus Temperatures of Palladium 40%
Nickel Alloy ASG**

Lab	Equipment	Crucibles	mass (mg)	Thermo- couple	Solidus Temp °C	Liquidus Temp °C
A	Stanton Redcroft DSC 1500	Platinum/ sapphire liners	48	Type R (Pt/13%Rh)	1231 $\pm$ 1.9 ^(a)	1230 $\pm$ 0.8 ^(a)
B	Netzsch 404	Alumina	49.1	Type S (Pt/10%Rh)	1250 $\pm$ 8.2 ^(a)	1239 $\pm$ 9.4 ^(a)
B1	Netzsch 404	Platinum/ sapphire liners	49.1	Type S (Pt/10%Rh)	1242 $\pm$ 2.4 ^(a)	1236 $\pm$ 5.5 ^(a)
C	Netzsch 404	Platinum/ alumina liners	47	Type S (Pt/10%Rh)	1235 $\pm$ 1.9 ^(a)	1228 $\pm$ 2.1 ^(a)
D	Netzsch 404	Platinum/ alumina liners	7.7	Type S (Pt/10%Rh)	1237 $\pm$ 0.4 ^(a)	1235 $\pm$ 0.7 ^(a)

Literature value for melting point 1237 °C^[2].

^(a) Standard deviation reported: σ_{n-1} .

Table 3
Measurement of Gamma-Delta Transformation of Iron ENL on heating and cooling

Lab	Equipment	Crucibles	mass (mg)	Thermo-couple Type	Heating onset °C	Cooling onset °C
A	Stanton Redcroft DSC 1500	Platinum/ sapphire liners	38	Type R (Pt/13%Rh)	1389 ± 0.8 ^(a)	(i)
B	Netzsch 404	Alumina	295.7	Type S (Pt/10%Rh)	1403 ± 2.5 ^(a)	1399 ± 0.8 ^(a)
C	Netzsch 404	Platinum/ alumina liners	128	Type S (Pt/10%Rh)	1391 ± 0.5 ^(a)	1355 ± 5.4 ^(a)
D	Netzsch 404	Platinum/ alumina liners	4.5	Type S (Pt/10%Rh)	1394 ± 1.0 ^(a)	1399 ± 0.7 ^(a)

Literature values for Gamma-Delta transformation 1392 °C^[3].
Heating and cooling rates 10 °C/min.
(i) Laboratory A observed a wide range of temperatures, up to 50 °C, for the transformation temperature on cooling. They preferred not to quote a result.
^(a)Standard deviation reported: σ_{n-1} .

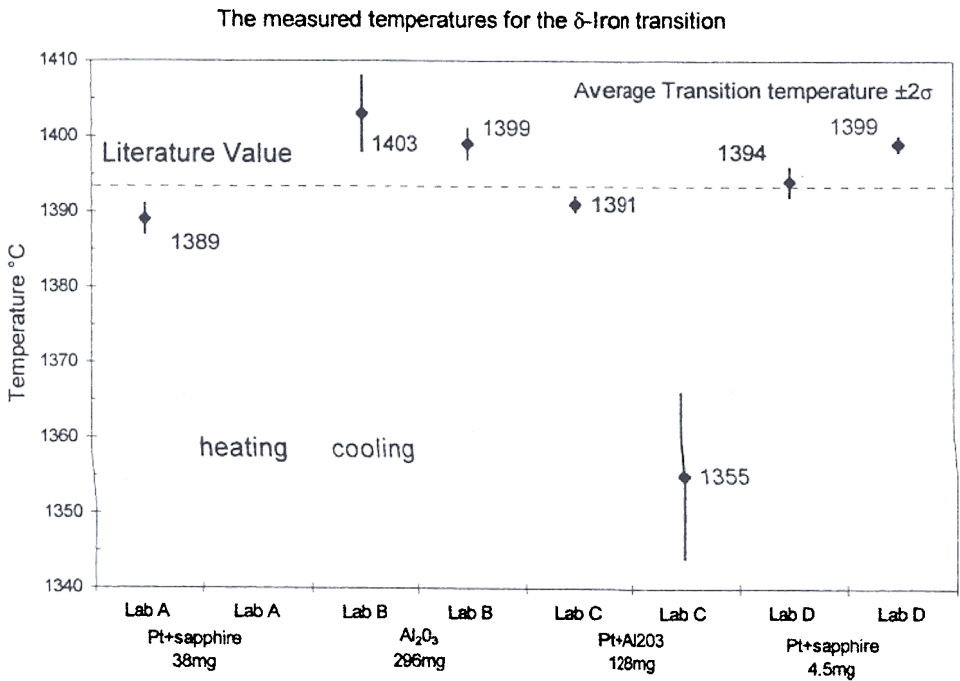


Figure 14 Measured temperatures for $\gamma \rightarrow \delta$ Fe transition as reported by different laboratories.

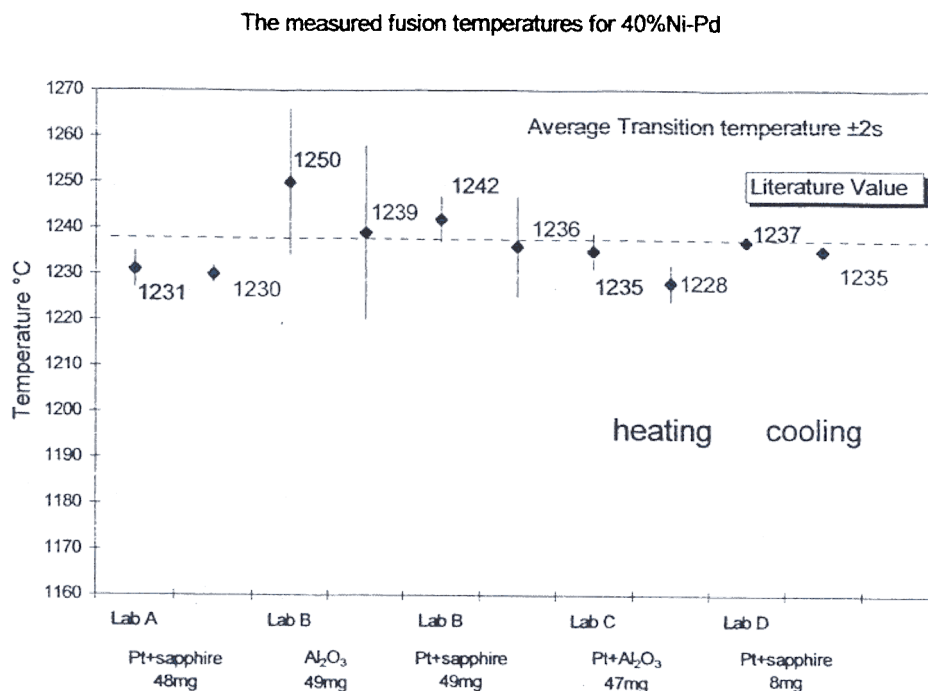


Figure 15 Measured temperature of minimum in melting for 40% Ni + 60% Pd alloy.

4 CONCLUSIONS

1. Two reference materials are recommended for the calibration of the temperature scale for DSC and DTA instruments, viz:
 - (i) (γ - δ) transition in pure Fe; $T_{\text{trans}} = 1392^\circ\text{C}$;
 - (ii) (40% Ni - 60% Pd) with a eutectic temperature of $1237 \pm 2^\circ\text{C}$.
2. Temperature corrections for the onset and peak temperatures have been determined for the NPL-DSC instrument; it is recommended that all instruments should be calibrated in a similar manner using the above calibrants and Cu and Ni.
3. It is recommended that small samples should be used for measurement of peak temperature.
4. This investigation has highlighted the effect that oxygen ingress can have on the melting point. As a consequence of this work it is recommended that for accurate, traceable measurements
 - (i) furnace tubes should be examined frequently to detect any cracks which may have occurred in the tube;

- (i) furnace tubes should be examined frequently to detect any cracks which may have occurred in the tube;
 - (ii) all plastic tubing in the DSC and the gas train should be replaced by stainless steel tubing and fittings;
 - (iii) great care should be taken to ensure that the fittings are gas tight and that the lines are free from moisture;
 - (iv) frequent checks should be carried out with the reference materials to ensure that the instrument is performing reliably and that there is no oxygen ingress;
 - (v) the insertion of an oxygen probe in the exit line of the gas train is also recommended.
5. Cooling cycle measurements are not recommended for temperature calibrations.
 6. Onset temperatures for reference materials are probably less vulnerable to errors than peak temperatures but both onset and peak temperatures are useful since they provide a route to solidus and liquidus temperatures, respectively, when carrying out DSC measurements on commercial alloys with an appreciable melting range.
 7. The results obtained for the Fe-Pd and Co-Pd systems in this study are not consistent with published phase diagram data and further work is recommended.

5 REFERENCES

1. Quested, P N, Mills, K C, Brooks, R F, Day, A P, Taylor, R, Szelagowski, H. "Physical Property Measurements for Simulation Modelling of Heat Transfer During Solidification", Proc. Amer. Vac. Soc. Conf., held Santa Fe, New Mexico, Feb 1997.
2. Massalski, T B. "Binary Alloy Phase Diagrams" 2nd Edition, ASM International, 1990, ISBN 0-87170-403X.
3. Dinsdale, A T. "SGTE Data for Pure Elements, CALPHAD, 1991, 15 (4) 319-427.
4. Hansen, M. "Constitution of Binary Alloys", McGraw-Hill, 1958, ISBN 07-026050-8.

FIGURE CAPTIONS

- Figure 1 Phase diagram of Fe-Pd system [3].
- Figure 2 Phase diagram for the Ni-Pd system [3].
- Figure 3 Phase diagram for the Co-Pd system [3].
- Figure 4 Schematic diagram showing the onset and peak temperatures during the heating cycle.
- Figure 5 DSC traces for pure Fe in the environment of the γ - δ transition with heating and cooling rates of 10 Kmin⁻¹.
- Figure 6 DSC traces for 30% Fe + 70% Pd for heating and cooling rates of 10 Kmin⁻¹.
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- Figure 8 DSC traces for 38.5% Co + 61.5% Pd for heating and cooling rates of 10 Kmin⁻¹.
- Figure 9 DSC traces for pure Al using heating and cooling rates of 10 Kmin⁻¹.
- Figure 10 DSC traces for pure Au using heating and cooling rates of 10 Kmin⁻¹.
- Figure 11 DSC traces for pure Cu using heating and cooling rates of 10 Kmin⁻¹.
- Figure 12 DSC traces for pure Ni using heating and cooling rates of 10 Kmin⁻¹.
- Figure 13 Corrections ($T_{\text{meas}} - T_{\text{lit}}$) for onset and peak temperatures for various calibrants as a function of temperature when using a heating rate of 10 Kmin⁻¹; X, onset temperature; O, peak temperature.
- Figure 14 Measured temperatures for $\gamma \rightarrow \delta$ Fe transition as reported by different laboratories.
- Figure 15 Measured temperature of minimum in melting for 40% Ni + 60% Pd alloy.