Application of high temperature DSC technique to nickel based superalloys

L. A. CHAPMAN
NPL Materials Centre, National Physical Laboratory, Teddington TW11 0LW, UK
E-mail: lindsay.chapman@npl.co.uk

Heat capacity is a critical input parameter in mathematical models of solidification and casting. It appears in its own right, and is required for the extraction of thermal conductivity from thermal diffusivity data. It also provides a measure of the latent heat associated with changes of phase, and the precipitation or dissolution of precipitates. Calorimetry is a well-established technique and is used to solve a wide range of materials problems such as studying precipitation or phase changes in alloy systems, and the kinetics of these phase transformations. The quality and range of data that can be obtained will be demonstrated by applying it to nickel base superalloys.

This paper discusses important aspects of the measurement including control of the atmosphere, suitable reference materials for temperature and enthalpy calibration, size of the sample and the rate of heating and cooling. The optimised DSC technique was used to investigate the properties of two nickel based superalloys (CMSX4 and IN738LC), comparing the results with previous values and determining sources of error in the method. © *2004 Kluwer Academic Publishers*

1. Introduction

The need for reliable data on thermophysical properties grows continually, both for modelling purposes and for the control of advanced solidification processes, in order to develop processing routes and increase efficiency. Knowledge of solidification behaviour is both theoretically and industrially important, as it is essential for the control of the casting process. In particular, knowledge of the latent heat of solidification is essential for the design of gating, risering, continuous casting and for the production of composite materials by solidification methods [1]. Any solidification model is only as good as the underlying data, which means that there is great demand for thermophysical property data, such as heat capacity (C_p), which is a critical property for solidification and casting models, appearing in its own right, and in expressions for thermal conductivity. Existing property data are sometimes only available for selected pure elements and a few simple alloys and compounds [2] and often the techniques available for their measurement are subject to considerable uncertainty [1, 3]. This has an impact on the reliability of thermodynamic models, which give a basis for predicting C_p.

For highly complex materials a complete thermodynamic description of the system involves a huge amount of work, and the predicted values often differ from those measured. In order to withstand the arduous conditions in a gas turbine engine, nickel based superalloys generally have complex compositions and small changes in composition can radically affect the properties. As industry moved towards a need for ever more efficient engines with higher operating temperatures, alloys were investigated that could be used at an increasing fraction of their melting temperature. The various properties that make these alloys suitable for such conditions, i.e. the high melting point temperature, mean that studies of the thermophysical properties have to take place at elevated temperatures, reducing the number of experimental techniques available [4–6].

The technique of Differential Scanning Calorimetry (DSC) was selected for the detailed study of nickel based superalloys. This is a well-established technique and is used to solve a wide range of materials problems such as studying precipitation or phase changes in alloy systems, and the kinetics of these phase transformations. The simplicity of the DSC technique and the general availability of the apparatus make it an economical method of obtaining temperatures of reactions. The energy change that is detected is often the latent heat for melting or a phase change. Methods of quantifying the measurement of this energy lead to improved knowledge about the chemical and microstructural changes occurring in the material and therefore assist with its optimisation through processing [3, 7–10]. In this work particular attention has been given to the areas of uncertainty, namely: calibration procedures; effect of environment (atmosphere control and containment of samples); specimen size; heating/cooling rate.

The calibration of the temperature scale must involve the application of reasonable calibration procedures, and the calibrant materials must be traceable [11]. The substances that are used should relate to the International Temperature Scale 1990. They must also possess the following features: be available in high purity form;

be chemically and physically stable; be easy to handle and of low toxicity; be well defined thermodynamically. Although pure metals fulfil most of these needs, there is a gap in the range 1100–1400°C. The use of binary Pd alloys and the γ-δ transition in iron have been successfully used to calibrate in this important range [12].

1.1. Effect of environment

A significant difficulty in high temperature work is preventing reactions which will contaminate the sample, and in particular reactions with the crucible. Metallic crucibles cannot be used as they are likely to diffuse into the alloy. Ceramic crucibles such as alumina, may react slightly, but are, in general, more stable. Unfortunately, at high temperatures, alumina is transparent to IR radiation, causing heat losses, and measurements become dependent on the emissivity of the sample. To overcome this, the author places a sapphire crucible inside an IR opaque platinum crucible. Slight reactions between the sapphire and the metal ensure some wetting of the crucible, which is necessary to ensure good thermal contact with the sensor. The use of a platinum crucible also ensures good thermal contact with the platinum sensor plate. However, this must be approached cautiously, as the platinum crucibles can become diffusion-bonded to the platinum plate, which ensures excellent thermal contact, but endangers the entire DSC head if a sample leaks. A sapphire disc between the crucible and the flux plate retains adequate thermal contact but also allows the platinum crucibles to be removed [12]. The slight degradation of the signal due to the thermal resistance of the sapphire is normally acceptable.

1.2. Oxidation

A further reaction, which must be controlled, is that with the atmosphere, which most commonly will result in oxidation of the sample. Oxidation causes signal noise in the data, which can obscure small phase transformations, and can change transition temperatures. Oxidation can affect both the sample and the sensor, so it is normal to use an inert shielding gas such as argon to minimise any degradation. For further improvement, measures should be taken to further purify the test cell atmosphere. Various methods of improving the transport of the gas to the sample chamber have been described [12, 13] but another solution is to improve the purity of the gas being used [12–14]. Consideration must also be given to the exhaust from the equipment, to prevent the possibility of back diffusion of oxygen [12, 13]. The use of an oxygen dependent transition such as the γ-δ phase transformation in iron may be used to test the atmosphere.

1.3. Effects of cooling rate

When using DSC to find the transition temperatures, Cp and enthalpy of an alloy, it is necessary to choose what heating and cooling rate to use. It is not possible, with the current instrument, to replicate the extremely fast cooling rates experienced in a casting (which could be potentially hundreds of degrees Celsius in a second), but as a guide to the melting range it works very well. Any calibration is only valid for the particular heating rate at which it was carried out, largely because the sensors in any DSC are relatively remote from the sample and thus a thermal gradient may be in effect between the sample and the sensor.

When different ramp rates are used, different transition temperatures may be observed. This can be corrected for by testing several heating rates and then extrapolating back to zero heating rate [11]. It should be noted that the use of different cooling rates can change the microstructure of a sample, such as the formation of a martensitic structure on quenching. One of the challenges of using the DSC is determining what is an instrumental effect and what is an actual thermal event due to changes in the sample. The standard heating rate used by the author is 10°C/min as this gives good resolution without being subject to picking up inordinate amounts of noise.

1.3.1. Sample size

If large samples are used at slow heating rates the temperature errors may be minimised [15]. Slower heating rates mean that equilibrium is reached, but a compromise must be arrived at because if rates are too slow the peaks produced may not be observable [8]. Similarly, large samples are prone to internal temperature gradients, which must be minimised to ensure that phase transitions occur simultaneously throughout the specimen. The size of the sample used depends on the design of the instrumentation. Burton [8] and Devletian [13] describe the optimum sizes for their individual techniques.

1.4. Metallurgy of superalloys

The phase reactions that occur in these highly alloyed materials play a crucial rôle in many aspects of the processing and service of high-strength nickel-based superalloys [3, 10]. Nickel based alloys have a face centred cubic (fcc) structure, very similar to that of stainless steel. This matrix is named the gamma (γ) phase, and has a large solubility for many elements [22, 24] but it contained a precipitated phase which was not identified until the 1940's. This precipitate consists of ordered intermetallic particles such as Ni_3Al (where the Al can be substituted by Ti, Nb or Ta). This is known as gamma prime, γ', and the remarkable properties of Ni base superalloys are due to the combination γ/γ' microstructure [14, 23, 24]. Gamma prime has an ordered fcc structure and is a close match with the matrix. This means that it precipitates evenly through the matrix and enjoys long-term stability [14, 22]. The amount of γ' present is critical to the performance of the superalloy, but it is dependent on temperature. The structure of superalloys is chemically dynamic, even at room temperature, and can only be observed temporarily [5]. Not only does the amount of γ' depend on the temperature at which the material is cast or wrought, but the
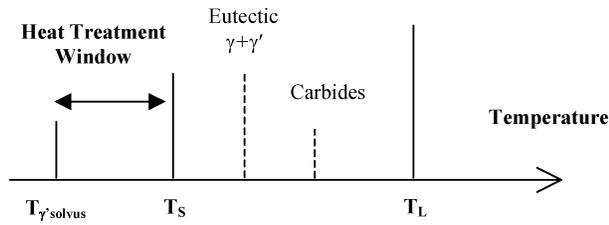
Figure 1 Schematic of transition temperatures in nickel-based superalloys. Solid lines signify transitions that are easily recognised; the transition temperatures represented by the dotted lines are more difficult to distinguish from the curves.

material is also reacting when the superalloys are exposed to the high temperatures of operation. The size and spacing of the γ' precipitates is also critical, and is a function of the processing conditions used, so for any given alloy the optimum properties are achieved only by using an appropriate heat treatment [23]. The precipitation of γ' in the matrix is a continuous process: the phases are constantly reacting and interacting. There are three main stages to precipitation, the nucleation of the precipitate γ' in the γ matrix, followed by growth and then ripening, or ageing. The energy required for nucleation of γ' from the matrix is low and so precipitation occurs easily as the temperature of the alloy falls [24, 25].

1.5. Importance of temperature measurement

It is crucial to identify the temperatures at which transformations take place in nickel-based superalloys because of the need to optimise the properties of the alloy. Many phase reactions in superalloys, including melting, occur over a temperature range rather than at a unique point. For nickel-based superalloys a balance has to be struck between the solidus temperature (the onset of incipient melting) and the solvus temperature (the temperature at which precipitation (of γ') begins). The temperature between these two features of the material is known as the heat treatment window (shown in Fig. 1). The incipient melting temperature is of high importance for post-casting heat treatment, because you want to maximise the amount of γ' present without introducing interdendritic liquid, as even small amounts of liquid cause problems with the workability of superalloys. In the production of directionally solidified (DS) or single crystal (SX) superalloys the solidus and liquidus temperatures are particularly important parameters, because of the need to begin withdrawing the furnace once solidification has begun. The solvus temperature is important because of the need to control heat treatment temperatures prior to precipitation hardening for castings, and in the control

of solutioning temperatures for hot working. The higher the γ' solvus temperature becomes, the greater is the necessity to try to increase the incipient melting temperature in order to conserve the solution heat treatment window, which has been found to be between 0 to 71°C in width [10, 14, 24].

1.5.1. Determination of transition temperatures

Sponseller [10] found that by Differential Thermal Analysis (DTA) it was possible to measure the γ' solvus temperature in nickel-based superalloys, on both heating and cooling cycles. This complements the work of Burton [8], who made measurements on cooling whilst investigating the effects of minor alloying additions on the phase changes of nickel-based superalloys. However, difficulties were observed by Wang *et al.* [3] in obtaining a value for the eutectic transformation temperature. Banerjee [7] compared predicted values obtained with a model with results obtained experimentally by DTA, in order to make adjustments to the model to allow for heat transfer coefficients. Undercooling of nickel superalloys has been observed by many workers, varying from sample to sample by up to 23°C [8, 10].

2. Experimental
2.1. Materials
The development of nickel-based superalloys was reviewed, and certain alloys (CMSX4 and IN738LC) were selected to relate their composition (given in Table I) to specific heat measured by the DSC technique.

CMSX4 is an example of an advanced nickel based alloy used in the production of single crystal turbine blades. It contains a high concentration of refractory elements, only minimal carbon and is characterised by a high gamma prime solvus temperature.

IN738LC is an example of an alloy used in industrial gas turbine engines where corrosion resistance is important. It is characterised by high chromium content and a lower gamma prime solvus temperature. The carbon produces intermetallic carbides that form between the liquidus and solidus temperatures.

2.2. DSC method
Differential Scanning Calorimetry (DSC) is similar in principle to the basic DTA technique [2]. Two identical pans are heated and cooled by controlling the furnace temperature programme and the difference in temperature between the pan containing the sample

T A B L E I The composition of the nickel superalloys investigated

Alloying element	Co	Cr	Ta	W	Al	Re	Ti	Mo	Si	C	Fe	Nb	B	Zr	Mn	Cu	Ni
CMSX4 (PHB)	9.7	6.4	6.5	6.4	5.6	3	1.1	0.6	0.4	0	0	–	–	–	–	–	Bal.
IN738LC (PGA)	8.3	15.9	1.7	2.6	3.5	–	3.5	1.7	0	0.1	0	0.8	0	0	0	<0.01	Bal.

and the other pan is recorded. The difference is measured as a function of temperature by means of thermocouples placed near the sample and reference pans. When a thermal event (such as melting) occurs the temperature of a pure element will remain constant until the transition is complete. The reference (empty) pan will continue to change in temperature according to the controlled programme, which leads to a rapid change in the temperature difference between the two pans.

2.2.1. Ratio method for calculating C_p

The results for specific heat measured in this investigation were calculated from raw data files using the ratio method. The basic equation is as follows [15]:

$$C_{ps} = [(S_s - S_e)/(S_c - S_e)] \cdot [m_c/m_s] \cdot C_{pc} \quad (1)$$

where C_{px} = specific heat of specimen, x; S_x = signal of specimen, x; m_x = mass of specimen, x; $x = s$ (sample), c (calibrant), e (empty).

The ratio method of determining specific heat relies on measuring a calibrant of known specific heat and mass to compare with the "unknown" sample. The calibrant should be a well-characterised material and if possible a certified reference material should be used [16]. The specific heat of a calibrant must be known to within an accuracy of 0.5% and should have been measured by two different adiabatic calorimeters. The use of a single grain (crystal, particle) of calibrant material is advised to ensure that multiple peaks are not observed [11]. In the temperature range 25–2000°C the heat capacity standard is α-alumina, synthetic sapphire [16–18].

Once the empty, calibrant and specimen data have been chosen, the software can be used to calculate the specific heat, using a polynomial value for the specific heat of the sapphire runs [16–19].

2.2.2. High temperature operation

The DSC unit has been modified for high temperature operation by fitting stainless steel gas lines throughout, and adding a commercial gas purification train to reduce the effects of oxygen, moisture and other possible contaminants. A one way (Bunsen) valve prevents ingress of oxygen from the exhaust.

3. Results
3.1. Heating/cooling rates
3.1.1. Temperature calibration

In order to determine the effect of ramp rate on the measurements, temperature calibrations were made at different rates with fresh samples of nickel, to reduce the risk of sample degradation.

The results of the temperature calibrations, and their extrapolation to zero ramp rate are given in Table II.

H Extrap. is a value obtained by extrapolating the liquid baseline until it meets with the slope of the back of the transition peak. Where the two extrapolated lines

TABLE II Transition temperatures for nickel on heating and cooling

	Heating				Cooling		
H Onset	H Peak	H Extrap.	H Offset	Rate (°C/min)	C Onset	C Peak	C Offset
1447	1477	1494	–	40	1417	1401	1344
1448	1479	1492	1500	20	1427	1412	1382
1435	1459	1464	1469	10	1378	1385	1363
1444	1462	1467	1470	5	1396	1401	1387
1443	1455	1458	1459	2	1417	1421	1412
1443	1451	1453	1454	1	1403	1412	1400
1443	1457	1459	1455	zero	1530	1536	1523

meet is the extrapolated offset. It is often quoted as the completion of melting, because the true offset is influenced by the instrumental lag. Nickel is particularly susceptible to undercooling, with a temperature drop of 200°C not uncommon. An example of this variation is shown in Table II, at the 10°C/min heating rate there is a marked difference in the onset and peak values compared with the other rates. The literature value for the melting transition of nickel is 1455°C [20]. The question of using these results in order to calibrate the DSC for temperature purposes is whether it is the oxide transition that is being measured, or whether the temperature scale needs correcting by 2°C (using the peak temperature from the heating curves). This 2°C peak temperature is a correction equivalent to 0.14% of the transition temperature.

3.1.2. Measurements on a nickel based superalloy (CMSX4)

There has been a previous study carried out on one of the alloys of interest (CMSX4) using DSC equipment. The melting range is quoted as being from 1320 to 1380°C [21]. The composition of the sample of CMSX4 is given in Section 2.1.

3.1.3. Effect of heating rate on CMSX4

Armed with the information from changing the calibration heating rate (see Section 3.1.1), it was decided to test the effect of ramp rate on a nickel-based superalloy CMSX4 (PHB). Fig. 2 shows the results for CMSX4 having been heated at different ramp rates over the temperature range of 1000–1500°C. Unfortunately the 1°C/min measurements were so noisy that it was

TABLE III Summary of transition temperatures for CMSX4 with varying cooling rate

	Cooling runs			
Rate	Run	C Onset	C Peak	C Offset
40	Cp837	1324	1321	1245
20	CP838	1330	1327	1276
10	CP827	1344	1340	1284
5	CP840	1344	1341	1289
1	CP839	1355	1354	1295
zero	calc	1351	1348	1297

PHB CMSX4 various samples
Run on heating at different ramp rates

Legend:
- CMSX4, 40.0°C/min, 98.60 mg,
- CMSX4, 20.0°C/min, 96.30 mg,
- CMSX4, 10.0°C/min, 145.20 mg,
- CMSX4, 5.0°C/min, 98.80 mg,

Rate	Onset	Peak	Extrap	Offset
40	1330	1401	1417	1438
20	1318	1388	1398	1413
10	1308	1381	1388	1396
5	1312	1374	1378	1383
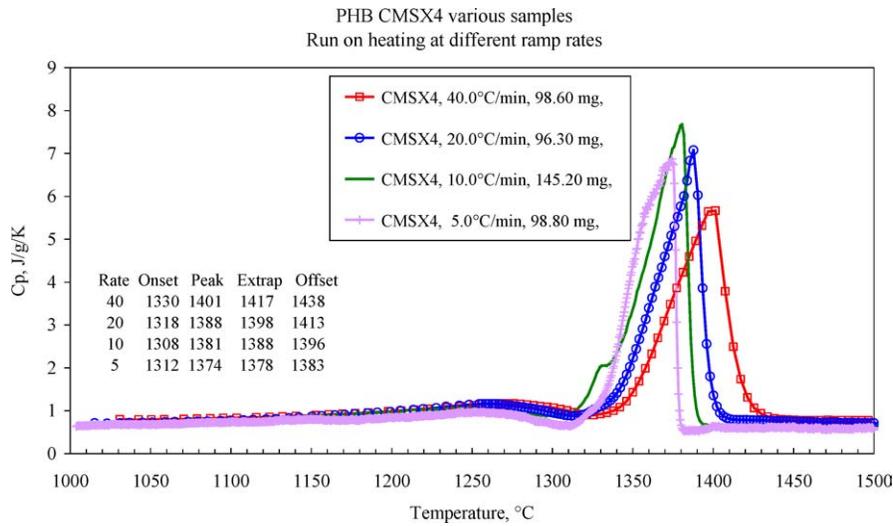
Figure 2 CMSX4 tested at different heating rates.

not possible to retrieve the melting range data from the signal. An interesting point to consider is that for the CMSX4, despite the changes in the transition temperatures, the Cp values are fairly consistent (Fig. 2). This was not so for the nickel, where the shapes of the Cp curves changed with heating rate.

On cooling it was possible to get a curve from the 1°C/min measurement and Table III shows the values obtained for the features of the CMSX4 transition with all the cooling rates.

3.1.4. Measurements on a nickel based superalloy (IN738LC)

This alloy was then given the same treatment as the alloy CMSX4, by testing samples at different ramp rates. The results on heating are shown in Fig. 3. The run at 1°C/min was again very noisy and it was difficult to ascertain the transition values.

During the cooling runs (shown in Fig. 4) at various ramp rates, the samples experienced undercooling on both the main transition peak and the secondary peak.

4. Discussion

Previous results obtained for CMSX4 using the same instrument, before the atmosphere was improved, were consulted before undertaking these new measurements, to give an idea of the temperature range in which to work. With the improvements made to the controlled atmosphere in the DSC (see Section 1.2) the results should be less influenced by oxidation than previous measurements.

The effect of the undercooling (supercooling) on the cooling curves is significant. For pure nickel this phenomenon can occur at 200°C below the literature value for the transition temperature. There is also a contribution due to the dynamic nature of the technique, which imposes a heating regime on the sample. Ideally a pure material should remain at one temperature while nucleation and initial growth of grains occurs, but in the DSC with a rapid reduction in temperature of its surroundings, this transition is suppressed, with the result that it happens rapidly at a lower temperature. This results in a sharp peak for a pure material, and a sharp onset followed by further transitions for an alloy material. This effect makes it difficult to determine
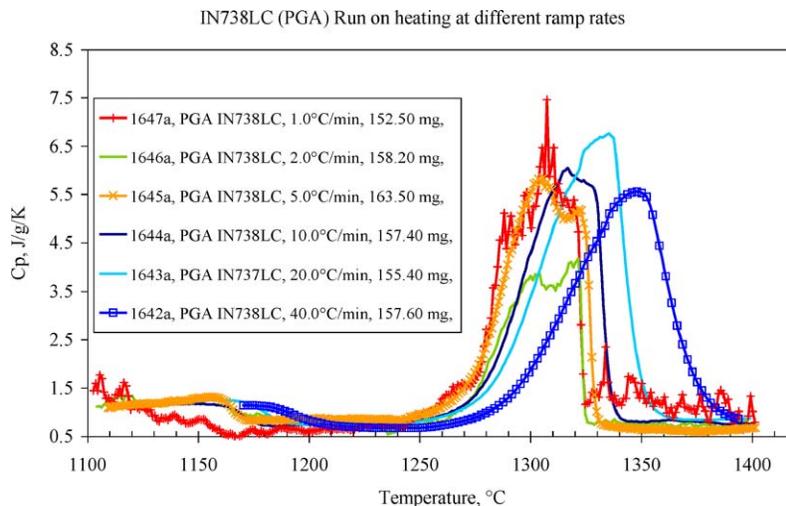

IN738LC (PGA) Run on heating at different ramp rates

Legend:
- 1647a, PGA IN738LC, 1.0°C/min, 152.50 mg,
- 1646a, PGA IN738LC, 2.0°C/min, 158.20 mg,
- 1645a, PGA IN738LC, 5.0°C/min, 163.50 mg,
- 1644a, PGA IN738LC, 10.0°C/min, 157.40 mg,
- 1643a, PGA IN737LC, 20.0°C/min, 155.40 mg,
- 1642a, PGA IN738LC, 40.0°C/min, 157.60 mg,

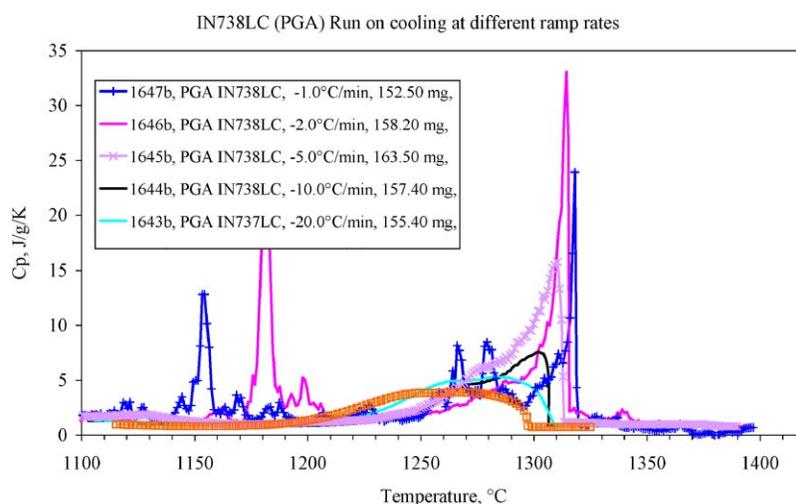*Figure 3* IN738LC Run on heating at different ramp rates.

7233

Figure 4 IN738LC Run on cooling at different ramp rates.

values for the enthalpy of a material, with both heating and cooling curves influenced by factors outside of the characteristics of the sample.

What was particularly unusual in the present results was that the values obtained on heating were lower than that for cooling. Usually a larger value would be obtained on heating, due to lag caused by the instrument smearing the liquidus temperature. The values for cooling are usually lower as the undercooling reduces any smearing effect. This may again be due to the many precipitates and different phases that are evolving during solidification. On heating the different phases may well dissolve slowly, as for the gamma prime dissolution. However in an undercooled system all of the transitions may occur at a temperature obscured by the main freezing curve, so in effect the sample is smearing its own results. The ideal way to measure enthalpy would be to hold the material at tiny temperature steps, and determine when the largest intake of heat occurs to maintain the temperature. However this is not a practical method (being time consuming and therefore expensive) and it is advisable to adapt a readily available method such as DSC, by considering the flaws of the technique and correcting for them. Any technique which held samples of CMSX4 at high temperature for a long time would lose elements such as chromium to the sample chamber, and would undergo a great deal of oxidation. The problem of oxidation was exacerbated when performing experiments at different ramp rates. At the slower ramp rates there were increased amounts of oxidation,

as a result of being held at higher temperatures for longer.

The alloy (CMSX4 PHB) showed signs of undercooling, which is not surprising considering the high nickel content and the results for pure nickel. There are a lack of nucleants such as carbides in the single crystal alloy, which would normally reduce undercooling. There is a relationship between the cooling rate and the amount of undercooling achieved: the slower the cooling rate, the less undercooling there will be. The slower ramp rates also gave a sharper undercooling peak, showing that the detection of the transition is better at the slower ramp rates. At the faster ramp rates the typical sharp undercooling peak is obscured by the rapid cooling of the furnace, and it gets smeared in a similar fashion to the offset temperatures on heating. However the signal from the slower ramp rates has increasing amounts of noise making it difficult to separate the beginning of a transition from the background signal.

Normally the heating runs are used to obtain the solidus, and the cooling runs are used to quote the liquidus. Therefore for this sample of CMSX4 the value of the solidus temperature should be 1306°C and a liquidus of 1351°C. However these have been affected by undercooling and so it may be more pertinent to use the values obtained on heating. There are arguments for using each of the different features of the heating curve as the completion of melting; a common practice is to use the main slope of the peak and note where it hits

TABLE IV Transition Temperatures for IN738LC with different ramp rates

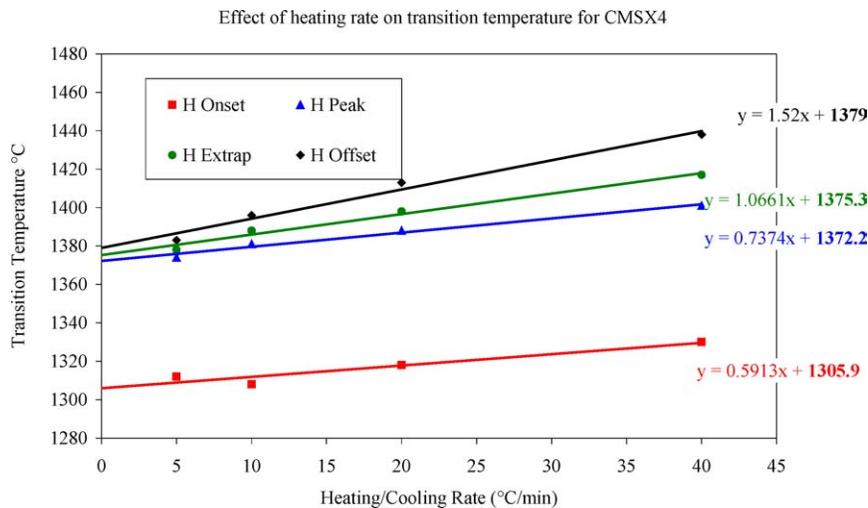| Heating					Cooling		
H Onset	H Peak	H Extrap.	H Offset	Rate	C Onset	C Peak	C Offset
1251	1348	1375	1390	40	1297	1271	1165
1240	1335	1349	1360	20	1309	1283	1165
1241	1318	1336	1341	10	1306	1302	1197
1240	1303	1329	1332	5	1313	1304	1214
1236	1321	1324	1326	2	1316	1314	1242
1243	1307	1324	1325	1	1320	1318	1250
1238	1309	1322	1324	zero (calc)	1317	1314	1233

Figure 5 Extrapolation to zero heating rate for IN738LC.

the extrapolated baseline. This reduces the influence of the instrumental lag and therefore smearing. The values obtained on heating PHB at different ramp rates are presented in Fig. 5, showing the trend for the peak and offset temperatures to converge as the slower heating rates are approached. These are summarised in Table IV.

When measuring a smaller transition such as a eutectic reaction, the DSC will only detect a transformation when the cumulative heat effect exceeds the detection limit of the instrument. These effects are often separated from other transitions on cooling, but these temperatures could be affected by undercooling.

5. Conclusion

Differential Scanning Calorimetry (DSC) is a commonly used method for the determination of thermophysical properties, due to being cheap and widely available. With care, it is possible to use the DSC to compare the transition features of different superalloys, with a view to finding the optimum heat treatment window.

At high temperatures it is especially important to monitor the ingress of oxygen to the instrument, and to consider the effects of any oxide on the material being investigated.

Care must also be taken when extracting data from the DSC to ensure that the effect of the instrument on the values obtained is minimal. This can be done by testing samples of different mass, and by measuring at different ramp rates and extrapolating back to a heating/cooling rate of zero. However this increases the complexity and cost of the measurement.

The influence of undercooling on a measurement must be recognised. Recommended values for CMSX4 code PHB, $T_{sol} = 1306°C$ and $T_{liq} = 1375°C$. The recommended values for IN738LC code PGA, after correcting to a zero heating rate are $T_{sol} = 1238°C$ and $T_{liq} = 1322°C$.

References
1. B. SARANGI, A. SARANGI, S. MISRA and H. S. RAY, *Thermochimica Acta* **196** (1992) 45.
2. K. D. MAGLIC, A. CEZAIRLIYAN and V. E. PELETSKY, "Compendium of Thermophysical Property Measurement Methods: 1 Survey of Measurement Techniques" (Plenum Press, New York, 1984).
3. H. P. WANG, J. AOU, E. M. PERRY and R. DOHERTY, "Investment Casting Solidification Simulation of Nickel-based Superalloys: Micromodelling Aspects" (Trans. of the American Foundrymen's Society, 1994) vol. 100, p. 771.
4. J. BETTERIDGE and W. HESLOP, "The Nimonic Alloys and Other Nickel Base High Temperature Alloys" (Edward-Arnold Bristol, ISBN 0 7131 3316, 1974).
5. C. T. SIMS, N. S. STOLOFF and W. C. HAGEL, "Superalloys II" (Wiley, New York, 1987).
6. Y. ZHU, S. ZHANG, T. ZHANG, J. ZHANG, Z. HU, X. XIO and C. SHI, "A New Way to Improve the Superalloys" (The Minerals, Metals and Materials Society, Superalloys, 1992).
7. D. K. BANERJEE, W. J. BOETTINGER, R. J. SCHAEFER and M. E. WILLIAMS, "Modelling of Heat Flow During Solidification and Melting in a Differential Thermal Analyser (DTA)," Modelling of Casting Welding and Advanced Solidification Processes VII (The Minerals, Metals and Materials Society, 1995).
8. C. J. BURTON, "Differential Thermal Analysis and The Mechanisms of Minor Additions in Superalloys," Superalloy Metallurgy and Manufacture Proc. 3rd International Symposium on Superalloys at Seven Springs, Sept. 1976.
9. S.-W. CHEN and S.-C. JENG, *Metall. Mater. Trans.* A **28A** (1997) 503.
10. D. L. SPONSELLER, *Superalloys* (1996) 259.
11. G. HÖHNE, W. HEMMINGER and H.-J. FLAMMERSHEIM, "Differential Scanning Calorimetry an Introduction for Practitioners," Springer 1996.
12. L. A. CHAPMAN, A. P. DAY and P. N. QUESTED, "Reference Materials for Calibration of Temperatures in DTA/DSC Instruments," NPL Report CMMT (A) 157, Feb. 1999.
13. Y. ZHU and J. H. DEVLETIAN, *Adv. Mater. Proc.* **140**(4) (1991) 51.

14. S. R. DHARWADKAR, K. HILPERT, F. SCHUBERT and V. VENGOPOL, *Z Metallkd* (1992) 10.

15. M. J. RICHARDSON, in "DSC on Polymers: Experimental Conditions," Calorimetry and Thermal Analysis of Polymers, edited by B. F. Mathet (Hanser/Gardner Publ. Inc., Feb. 1994).

16. J. E. CALLANAN, *J. Therm. Anal.* **45** (1995) 359.

17. ASTM Standard E968-83 (REAPPROVED 1993), "Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters."

18. P. LE PARLOUER, *Rev. Int. Hautes Temp. Refr.* Fr **28** (1992–1993) 101.

19. S. M. SARGE *et al.*, *Thermochimica Acta* **247** (1994) 129, Table 2, Col. b.

20. A. T. DINSDALE, *CALPHAD* (4) (1991) 319.

21. K. C. MILLS, "Recommended Values of Thermophysical Properties for Selected Commercial Alloys" (Woodhead Publishing Ltd., 2002) p. 167.

22. R. BOWMAN, "Superalloys: A Primer and History," 2000. http://www.tms.org/Meetings/Specialty/Superalloys2000/ SuperalloysHistory.html

23. M. P. JACKSON and R. C. REED, "Determination of the Precipitation Kinetics of Ni3Al in the Ni-Al System Using Differential Scanning Calorimetry," submitted for publication to Metall and Mat. Trans.

24. M. DURAND-CHARRE, "The Microstructure of Superalloys" (Gordon and Breach Science Publishers, Amsterdam, 1997).

25. G. LAMANTHE, J. P. RIQUET and C. BERNARD, *Rev. Int. Hautes Temper. Refrat Fr.* **18** (1981) 265.

26. S. VYAZOVKIN, *Anal. Chem.* **74** (2002) 2749.

27. W. J. BOETTINGER and U. R. KATTNER, *Metall. Mater. Trans.* A **33**(6) (2002) 1779.