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Some Practical Considerations for High Temperature DSC

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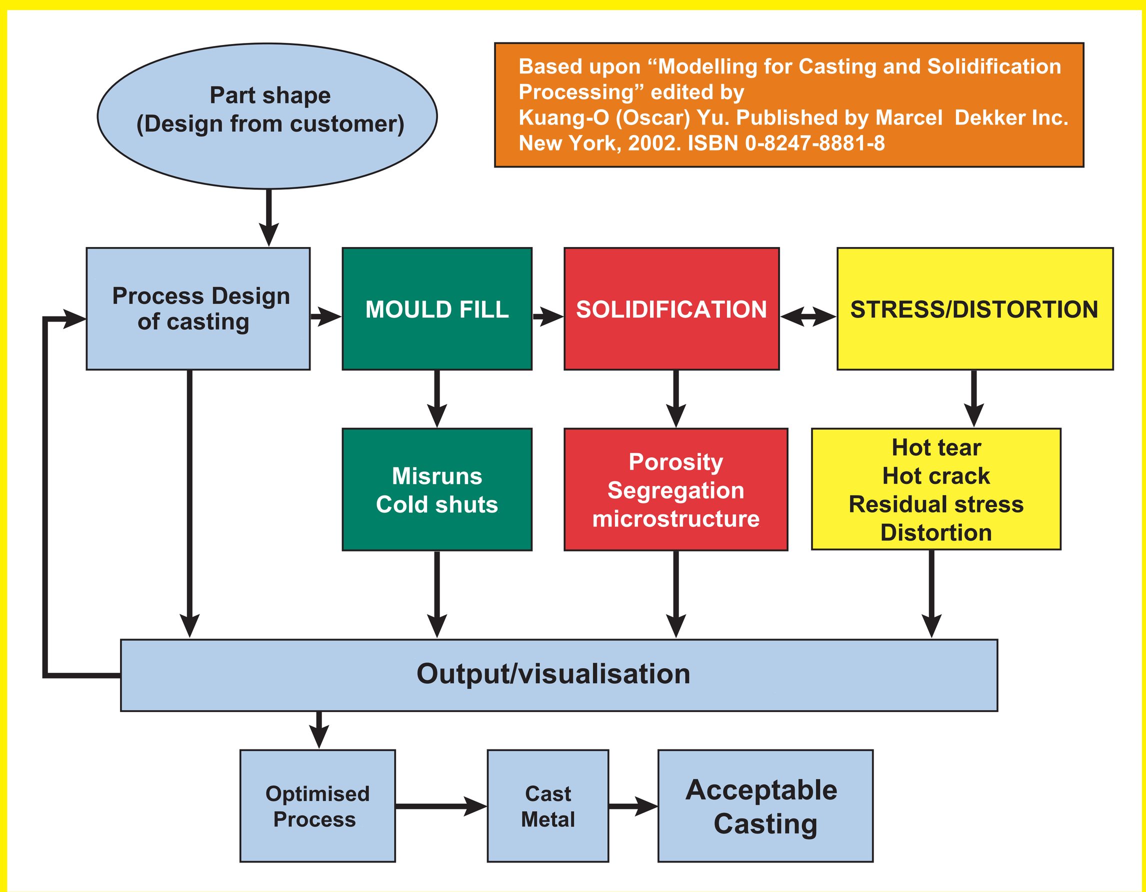
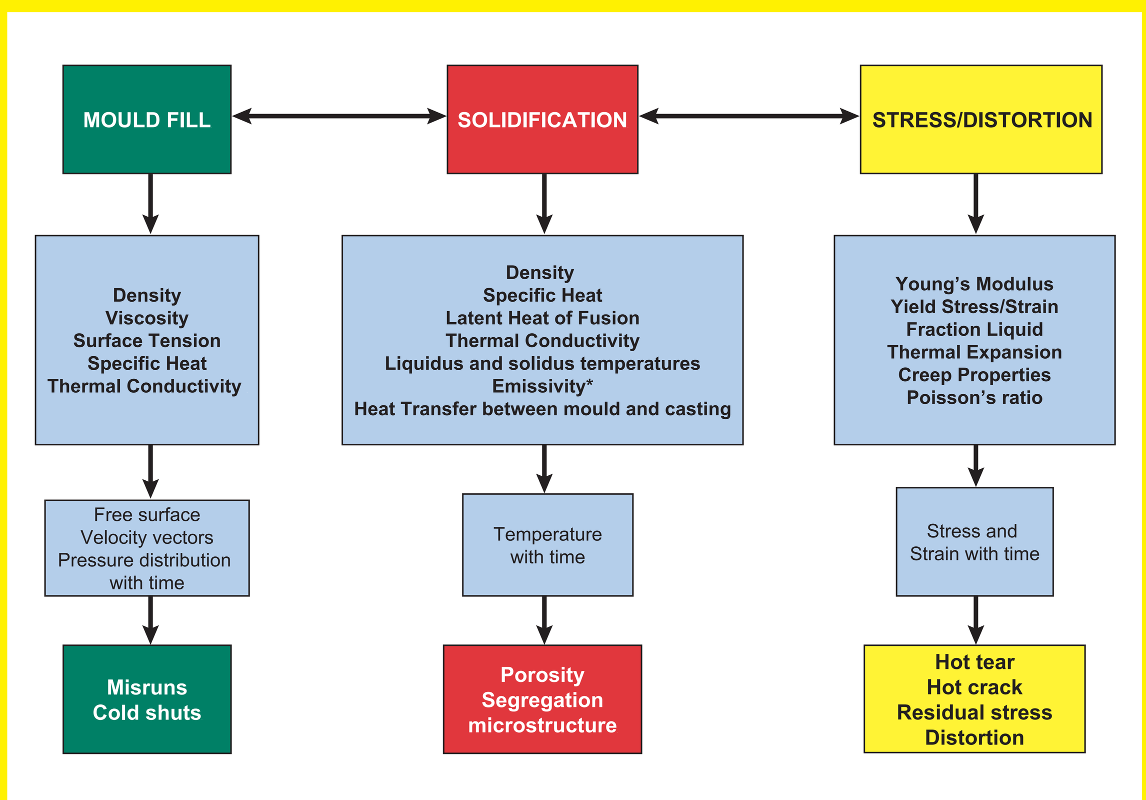
Industry regularly uses prediction software to simulate their processes

- Freezing range, specific heat and enthalpy are particularly important to casting models
- **High temperature Differential Scanning Calorimetry** (DSC) is one method of obtaining these values
  - *Improvements to measurements save energy, money, time*
  - *Important aspects of the measurement include control of the atmosphere, suitable reference materials, size of the sample and heating / cooling rate*





High temperature DSC is used extensively for a number of applications:

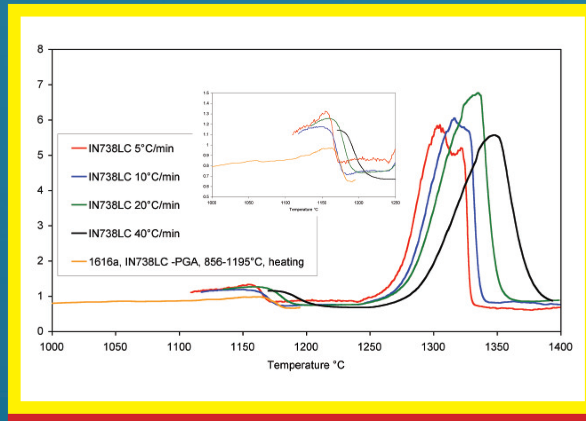
For example; extensive specific heat data for mould materials and metals is required to support solidification modelling, which is used extensively in the casting industry.

- Determining transition temperatures used for example in constructing phase diagrams and determining heat treatment schedules.
- Determining specific heats and enthalpy for modelling high temperature processes.
- Temperature changed at constant heating or cooling rate
- Usually 10 °C/min (range from 1 °C/min to 50 °C/min)
- Sample size of 10 mg – 350 mg
- Difference in signal between empty crucible and sample crucible is monitored

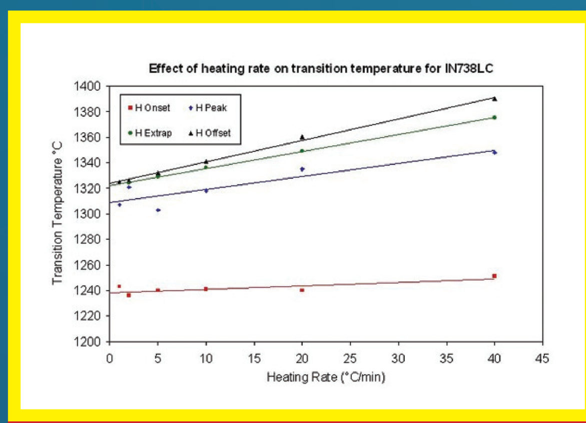
For successful DSC measurements at high temperature care is required:

- Suppressing reactions between the material and the metal crucible but maintaining reasonable contact between the materials measuring sensor
- At high temperatures it is important to monitor oxygen ingress to the instrument, and to consider the effects of any oxide on the material being investigated

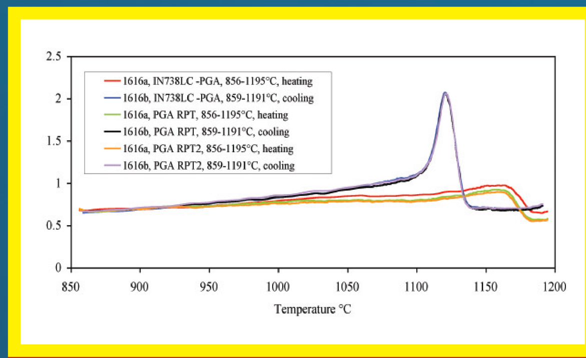
  Control of atmosphere. The source of argon is generally about 5 nines purity used for welding. There will be oxygen at up to tens of ppm and water vapour often picked up from the pipework.
- Deconvoluting the signal to allow for thermal lag between material and sensor
- Care must be taken when extracting DSC data 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
- Conventional DSC methods cannot easily resolve differences in closely spaced thermal events due to the smearing of data
- The influence of undercooling on a measurement must be recognised
- It is important to take into consideration any solid transitions when planning the temperature range, as these can affect later transition temperatures
- Calibration of temperature scale & heat capacity should be undertaken



Alloy measured at different heating rates



The effect of heating and cooling rates on transitions

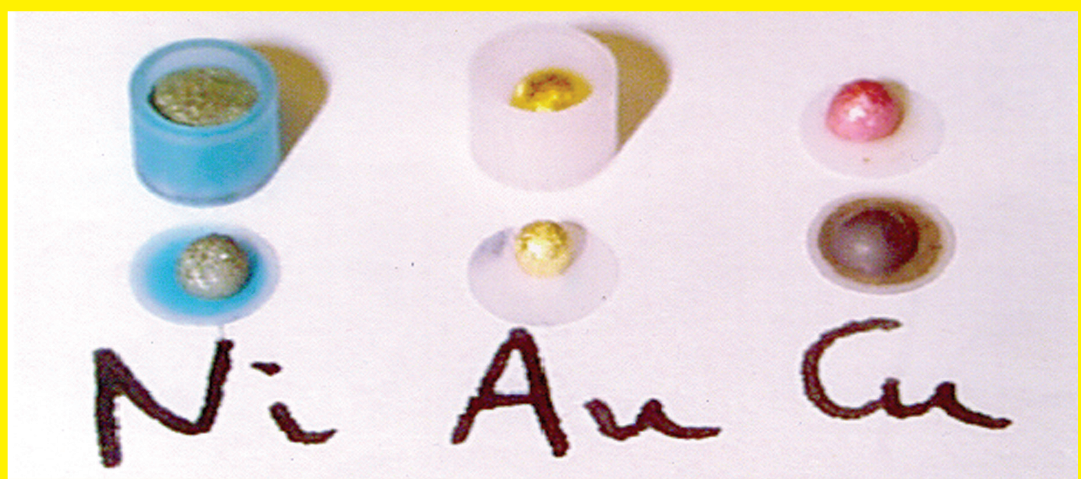


Dissolution of precipitate can effect later transition

Temperature Calibration

- Need accurate temperature measurement by DTSC
- Cannot measure in situ as have restricted space
- Solution: use well characterised materials as reference materials (pure materials that melt in required temperature range)
- Aluminium 660 °C
- Gold 1064 °C
- Copper 1084 °C
- Iron 1394 °C (and 1537 °C)
- Nickel 1455 °C
- Sapphire for specific heat capacity calibration
- None are really satisfactory

Calibration Observations



Calibration materials showing how gold spherodises

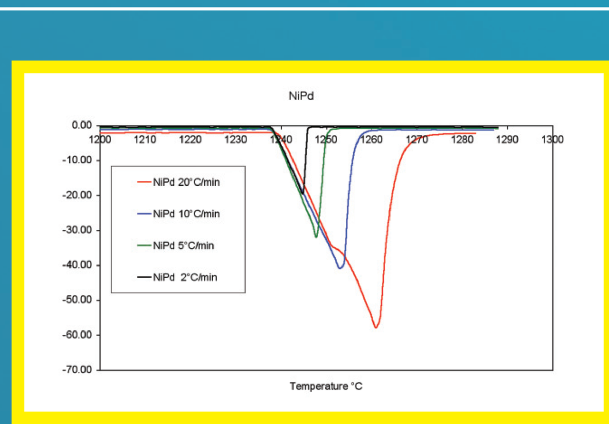
For example:

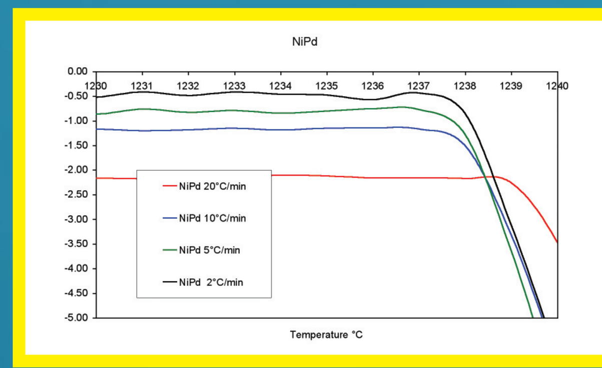
Au tends to spherodise and have poor thermal contact with the pan.

Ni is notorious for displaying undercooling although a small amount of a nucleant such as TiC reduces the effect. Also susceptible to oxidation and effecting the temperature.

Alternative Calibration Materials

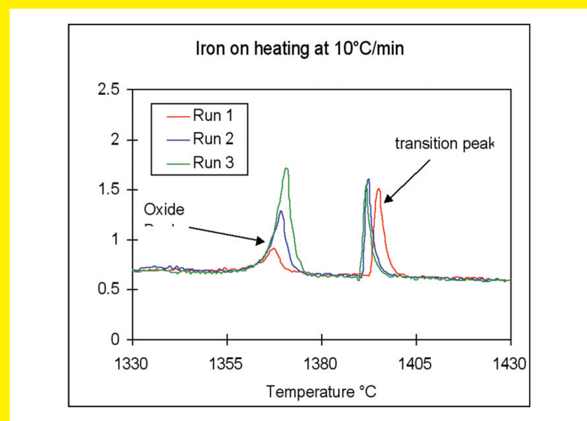
- Alternative reference materials have been investigated, including the δ-transition of iron and the melting point of a NiPd alloy (Trans 1237 °C)
- Also investigating a Co-C eutectic with M Pt of 1325 °C.
  This is a potential new fixed point and the temperature is measured to better than 200 mK by radiation pyrometry





Initial Iron Results – Oxygen Ingress

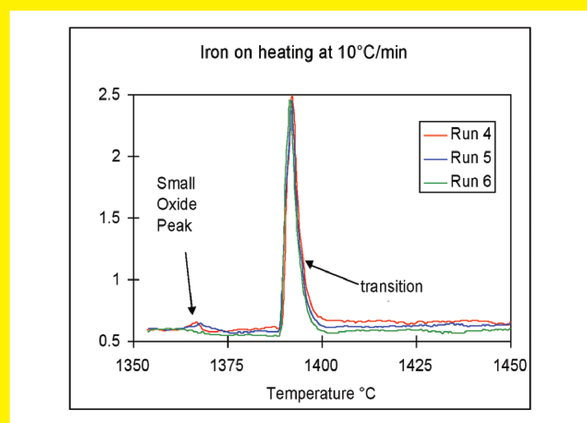
- Iron δ-transition (1394 °C)
- Larger specimens show greater undercooling
- Values affected by presence of second phase, probably oxide (extra peak)
- Second Peak in iron results due to oxide in samples
- Need better atmosphere control, can then reduce affect of oxygen in the system



Improved Iron Results

Improvements Made

- Reconditioned Furnace Installed (alumina sleeve over base of furnace tube)
- Stainless Steel Gas lines installed to replace nylon
  - *one way flow valve fitted*
  - *gas fittings generally improved*
- Added gas purification system to gas line
- Removal of oxygen, moisture and organics from gas cylinder



The reduction of the oxide peak and the reproducible temperature for the delta iron transition demonstrate the efficacy of the precautions taken to control the atmosphere.

The use of thin sapphire liners prevent the reaction of the metal with the platinum crucible and minimise the thermal lag on the temperature sensor.

Deconvolution programmes are required for desmearing curves if there are large changes such as melting and solidification.

Conclusions

1) O_2 can be controlled with relatively simple scrubbing techniques and improving tubing.
2) Sapphire inserts for many systems are sufficient to prevent reaction between crucible and material. Some reduction in heat transfer.
3) Temperature calibration needs refining. The melting point of elements is limited. δ Fe or NiPd are seen to be good. The direct uptake of Co-C which will hopefully be defined by the ITS scale needs investigating.
4) The position of the peaks is effected by the rate of heating or cooling. Extrapolation of the peak positions to zero heating rate is a good first approximation.

More complex deconvolution may be required.

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