

A NUMERICAL MODEL OF A TWO-PAN HEAT FLUX DSC

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Abstract

A numerical program has been written to treat a heat-flux DSC. The model operates in two modes. In the first, experimental data is used as input and the enthalpy is calculated as a function of the sample temperature rather than the sample thermocouple temperature. This allows accurate enthalpies and transition temperatures to be obtained without smearing.

In the second mode, enthalpy is used as an input and the responses of the calorimeter are calculated. Using this mode it is possible to investigate the effects of sample size, heating rate and alloy composition. Non-equilibrium effects and difficulty in nucleation can also be included.

Keywords: enthalpy, heat capacity, heat flux DSC, numerical modeling

Introduction

A conventional heat flux DSC consists of a reference and sample pan contained in a constant temperature enclosure. The difference in temperature between the sample and reference represents a difference in heat flux to the two pans. When latent heat has been or is being evolved in a sample, two problems arise:

1. The measured temperature difference is not proportional to the difference in heat capacity between the sample and reference [1].
2. The sample thermocouples do not measure the temperature of the sample since large temperature difference rise between sample and sample thermocouple [2]. This leads to significant errors in apparent transition temperatures. Neglect of these effects leads to latent heat for a pure metal apparently being evolved over a range of temperatures. This effect is known as smearing [3].

To reduce these problems DSC manufacturers usually recommend using very small samples. Unfortunately small samples lead to greatly reduced counts and loss of accuracy in enthalpy and heat capacity measurement.

A numerical program has been written which treats the complete process and models heat flux within a calorimeter. This allows the enthalpy to be calculated as a function of sample temperature rather than sample thermocouple temperature for any size specimen.

The program can operate in two modes: in the first, data from a calorimeter is used as the input to the program and enthalpy and effective heat capacity are calcu-

lated as a function of the sample temperature; in the second, temperature and temperature differences or counts are predicted from a known variation of enthalpy against temperature. A thermodynamic package such as MTDATA [4] or a non-equilibrium solidification model such as ALLOY [5] can be used to give the enthalpy values.

As examples, the numerical model has been used to correct results and predict calorimeter responses in a Stanton Redcroft heat flux DSC, a TA Instruments DSC2010 and a Mettler Toledo DSC 821°.

The physical model

Calculations of heat flow show that temperature differences within a sample are negligible compared to those that occur at a boundary between two different regions of a calorimeter [6]. It is proposed that a heat flux DSC can be represented by a number of regions of uniform temperature surrounded by thermal resistances. This is similar to that suggested by references [7, 8] in their analytical models. A similar but simpler scheme was used by reference [9] for the analysis of a temperature modulated DSC. The present work differs from the previous work in that solutions are obtained numerically rather than analytically. This allows much more flexibility in the complexity of the model and to the type of input. A schematic diagram of a heat flux DSC is shown in Fig 1.

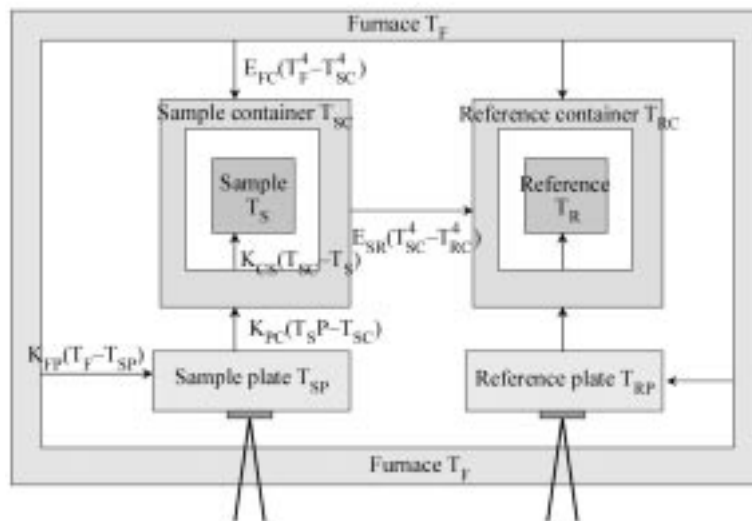


Fig. 1 A schematic diagram of a heat flux DSC showing the nine different heat fluxes being considered

Seven temperatures are either known or are calculated. These are the surroundings (or furnace temperature) T_f , the sample and reference plate temperatures T_{sp} and T_{rp} , the sample and reference container temperatures T_{sc} and T_{rc} , and the sample and

reference temperatures T_s and T_r . Subscript F is the surroundings (furnace), P the plates, C the containers and S and R refer to sample and reference.

Heat fluxes between the different regions are assumed to depend (Fig. 1), linearly on the temperature differences (conduction) or to depend on difference of the fourth power of the temperature difference (radiation). A heat balance equation can be written for each of the six different regions of the calorimeter. These are sample, reference, sample container, reference container, sample plate, reference plate. The equation for the sample container is:

$$m_{sc} C_{sc} (T_{sc} - T'_{sc}) = [K_{pc} (T_{sp} - T_{sc}) - K_{cs} (T_{sc} - T_s) + E_{fc} (T_f^4 - T_{sc}^4) - E_{sr} (T_{sc}^4 - T_{rc}^4)] \partial t$$

where m_{sc} is the sample container mass, c_{sc} the container specific heat capacity, T'_{sc} the container temperature at the start of the time step and ∂t the time step. The terms in K are effective heat transfer coefficients, and in E effective emissivities. The left hand side of the equation represents the change in enthalpy and the right hand side the sum of the fluxes. Similar equations can be written for the other five regions. The equations are solved fully implicitly. This means the change in temperature depends on fluxes calculated at the end of the time step. The method has the advantage that it is mathematically stable for any time step.

The method of solution is slightly different for the two different operational modes. In mode 1, when a corrected sample enthalpy is being calculated, a temperature and the temperature difference between the sample and reference thermocouple are given as a function of time. There are seven equations (the six equations plus the temperature difference) and seven unknowns (the six other temperatures and the enthalpy of the sample). This allows a consistent set of temperatures and sample enthalpy to be calculated.

In mode 2, when temperature differences are being calculated from a sample enthalpy temperature plot, one of the temperatures is scanned. There are again seven equations (the six equations plus a linearized equation for sample enthalpy vs. temperature) and the same seven unknowns. In practice it was necessary to repeat the calculation until the final enthalpy was interpolated between adjacent enthalpy temperature points rather than extrapolated from the equation existing at the start of the time step.

Since all the equations can be made linear they are solved using Gaussian elimination with partial rotation. The problem can be set up to include more or less regions and heat fluxes. The number chosen was selected as the minimum needed to be able to reproduce experimental calorimeter results. The number of heat transfer coefficients was kept small so that the values could be estimated reasonably easily from experiment. In practice the heat flow may be more complex than suggested in Fig. 1 if this is the case the K 's and E 's might be expected to vary slowly with temperature. Alternatively fluxes due to convection rather than radiation can be included for work at low temperatures.

Program operation

The program uses a Windows based environment where the calorimeter settings and experimental conditions can easily be investigated or changed. Figure 2 shows the start up screen. Values of the various heat transfer coefficients for a Stanton Redcourt heat flux DSC, Mettler Toledo DSC 821^e and a TA Instruments DSC2010 have been calculated and can be loaded from memory. The sample mass and heat capacity of the reference and containers are entered for each run. One of the two operational modes is then chosen. The calculated results can be plotted and exported as a text file.



Fig. 2 The 'Windows' start up screen for the numerical model

Calibration

The six heat transfer coefficients are reduced to three by assuming they are the same on the sample and reference side of the calorimeter. K_{FP} , K_{PC} and K_{CS} are the coefficients between the furnace and the plate, the plate and the container, the container and the sample. They are obtained using the experimental results for the melting and freezing of a pure material whose latent heat and heat capacities are known. Heating and cooling runs are carried out with isothermal plateaus of sufficient length to give good zero line corrections.

The heat transfer terms are set in an iterative procedure. The ratio of K_{FP}/K_{PC} is initially set to 1 and K_{FP} is adjusted until the calculated jump in the enthalpy plot is equivalent to the latent heat. The ratio K_{FP}/K_{PC} is then adjusted so that the enthalpy temperature plot becomes vertical at the melting temperature. The value of K_{CS} is then adjusted to ensure that the enthalpy plot is straight after melting or freezing. Finally the heat capacities in the solid and liquid are made correct by making small adjust-

ments to the mass of the reference plate. This adjustment is being used to offset any lack of symmetry in the calorimeter. The process is repeated until consistent results are obtained.

At present there is no reliable way of setting the emmissivity from the container to surroundings (E_{FC}). The value is set to zero or to a value where heat flow by radiation is just beginning to be significant at 600°C. The emmissivity term for radiation from the sample container to the reference container is taken to be the emissivity to the surroundings times the solid angle suspended by the sample over that for the surroundings. In practice emmissivities and heat transfer coefficients should be calibrated as close as possible to the temperature of application to minimize errors resulting from any change with temperature.

Enthalpy and heat capacity calculations

In this mode counts (temperature difference) and a temperature (T_{SP} , T_{RP} or T_F) as a function of time are read from the output of an experimental run. The run should include an isothermal plateau at the lowest and highest temperature of interest. These

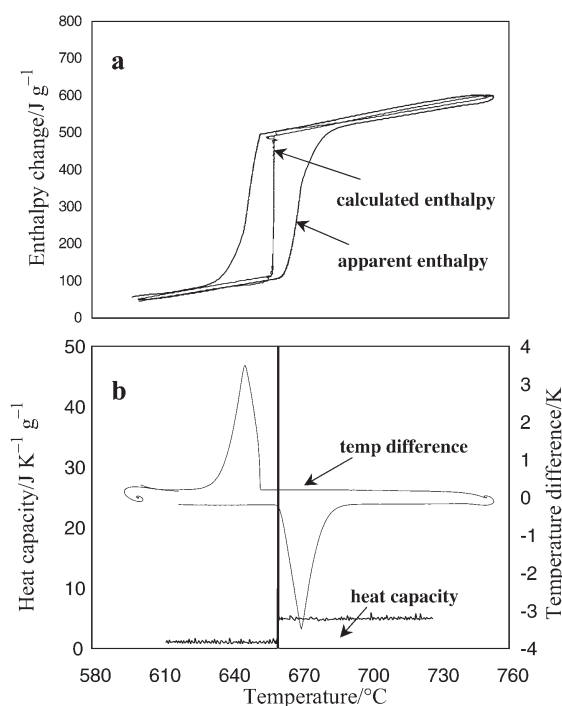


Fig. 3 10 mg pure Al sample heated/cooled at 10 K min⁻¹ in a Stanton Harcourt heat flux DSC. a – calculated enthalpy, and apparent enthalpy (enthalpy obtained by integrating counts), b – heat capacity and inputted temperature difference (temp. difference)

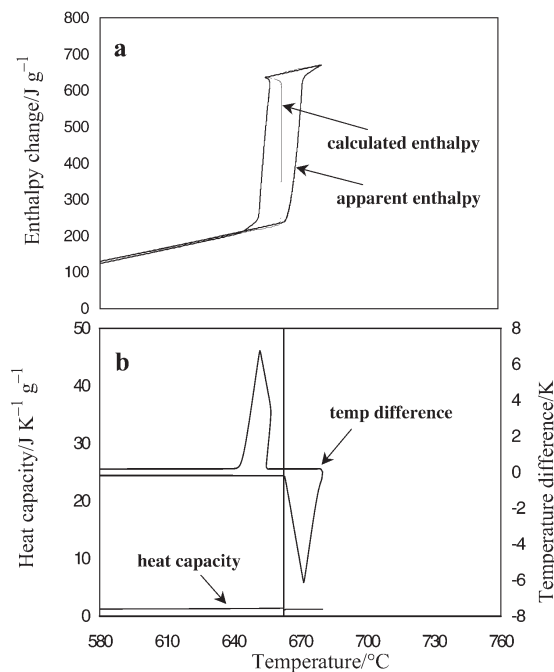


Fig. 4 10 mg pure Al sample heated/cooled at 10 K min^{-1} in a, Mettler Toledo DSC 821°. a – calculated enthalpy, and apparent enthalpy (enthalpy obtained by integrating counts), b – heat capacity and inputted temperature difference (temp. difference)

are used by the program to make a zero line correction [10]. The counts are then converted to temperature differences and fed into the calculation program to give enthalpy and effective heat capacity as a function of sample temperature as opposed to sample thermocouple temperature. The results can then be plotted as a function of time or temperature. As examples, the results from pure Al heated/cooled at 10 K min^{-1} in a Stanton Redcourt calorimeter, Mettler Toledo DSC 821° and TA Instruments DSC2010 are shown in Figs 3, 4 and 5. The sample size was 10 mg for the first 2 but 1.3 mg for the TA Instruments DSC2010. The samples are similar but not identical to those used for calibration. The calculated enthalpy is plotted against sample temperature as shown in Figs. As expected, the latent heat appears as vertical line on the Figs. The calculated enthalpy line should be compared with the apparent enthalpy line on the enthalpy plot, which show the enthalpy that would be obtained by integrating the counts and plotting the results against sample thermocouple temperature. On the lower diagrams the corrected heat capacity is plotted against sample temperature, and temperature difference between sample and reference thermocouple is plotted vs. sample thermocouple temperature. The heating and cooling curves on Fig. 5a do not coincide this is possibly the result of using a too small specimen; as might be expected more consistent results are obtained with larger samples. The im-

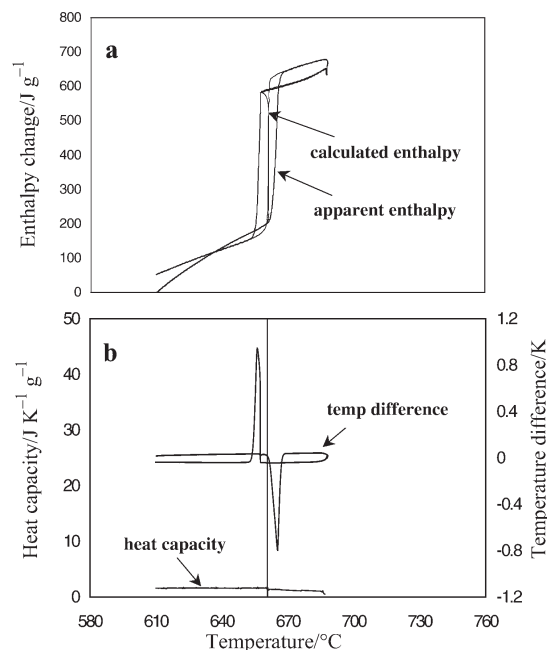


Fig. 5 1.3 mg pure Al sample heated/cooled at 10 K min^{-1} in a TA Instruments DSC2010. a – calculated enthalpy, and apparent enthalpy (enthalpy obtained by integrating counts), b – heat capacity and inputted temperature difference (temp. difference)

portant point is that whereas latent heat appears over a few tenths of degrees on the corrected plots it appears over about 20 K for 10 mg samples and 5 K for the 1.3 mg sample. Even the initial break in the beginning of melting is significantly different from the transition temperature using the sample temperature. It is interesting to note the effect of supercooling is readily apparent on the corrected enthalpy plot. The program can handle any form of input data including modulated DSC [11] results.

The predictive operational mode

In this mode enthalpy as a function of temperature is read from an external file. The initial data and data which is changed during the run is entered. The program is flexible and is able to reproduce any sequence of operations that can be programmed into a DSC. This includes scanning different thermocouples and modulated operation. Undercooling can be included to represent a difficulty in nucleating a new phase.

The results for a 2 mg sample pure Al sample heated at 5 K min^{-1} in a Mettler calorimeter are shown in Fig. 6. The sample temperature (T_s), sample plate temperature (T_{SP}), surroundings temperature (T_F) and the temperature difference (ΔT) are plotted as a function of time, in Fig. 6a. The temperature difference (counts) is plotted

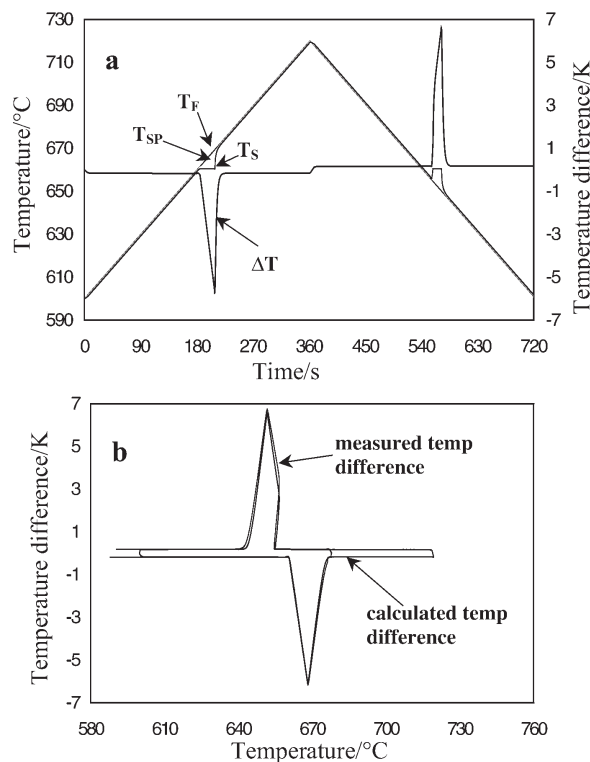


Fig. 6 Predicted results for a 2 mg pure Al sample heated/cooled at 5 K min^{-1} . A nucleation supercooling of 5 K has been included. a – Predicted sample temperature (T_S), sample plate (T_{SP}), surroundings temperature (T_F) and temperature difference (ΔT) plotted vs. time. b – Predicted and measured temperature differences plotted vs. temperature. The lines are almost superimposed

vs. sample plate temperature in Fig. 6b. This predicted plot is almost identical to the measured temperature difference also shown in Fig. 4b.

The program is useful, for example, for investigating the response of a calorimeter to sample size, rate of heating or type of alloy. Figure 7 shows the expected results for a 10 mg sample of an alloy (LM25) heated at 10 K min^{-1} in a TA Instruments DSC2010. The inputted enthalpy and predicted apparent enthalpy that would be calculated by integrating the counts were shown on Fig. 7a. The inputted heat capacity and the calculated temperature difference (counts) that would be expected were shown in Fig. 7b. From Fig. 7b it can be seen that the temperature difference is not proportional to the effective heat capacity when latent heat is evolved as is often assumed in the analysis of a heat flux DSC.

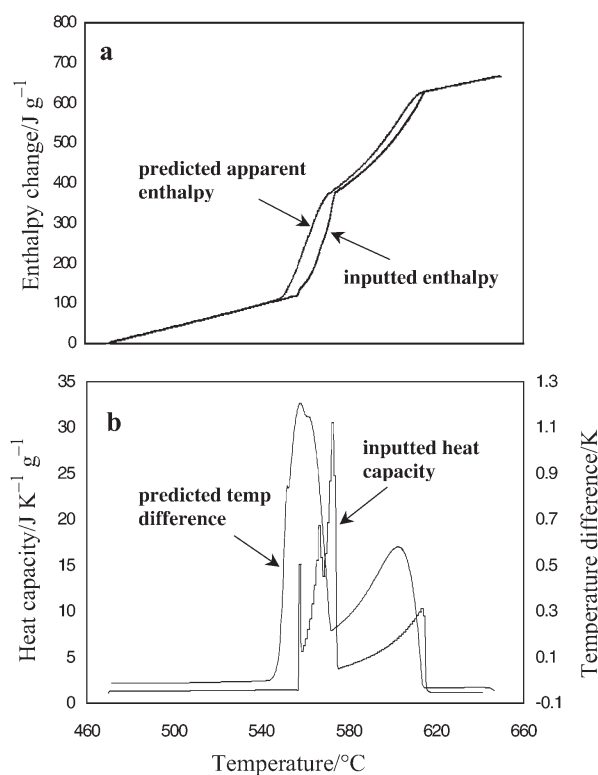


Fig. 7 The predicted results for a 10 mg sample of an alloy (LM25) heated at 4 K min^{-1} in a TA instrument DSC2000. a – The inputted enthalpy and predicted apparent enthalpy (integrated counts), b – The inputted heat capacity and the predicted temperature difference plotted vs. temperature

Conclusions

A numerical implementation of the approach suggested by [7, 9] has been implemented to model a heat flux DSC. In the correction mode the program can give accurate enthalpy and heat capacities from experimentally measured data. In the predictive mode it is possible to separate real kinetic effects in the sample from artifacts resulting from an oversimplified analysis of a heat flux DSC and the effect of sample size and heating rate can be examined.

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