

A NUMERICAL MODEL OF TWO-PAN HEAT FLUX DSC, WHICH ALLOWS
ACCURATE RESULTS TO BE CALCULATED FROM EXPERIMENT¹.

H. B. Dong^{2,3} and J. D. Hunt²

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² Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, U.K.

³ To whom correspondence should be addressed

ABSTRACT

A numerical model of a heat flux calorimeter has been developed. The model can be used in two different operational modes. In the first, experimental data from a heat flux calorimeter is used as input. The enthalpy and heat capacity is calculated as a function of sample temperature (rather than sample thermocouple temperature). This allows accurate enthalpies and transition temperatures to be obtained both for large and small samples.

In the second mode, enthalpy as a function of temperature is used as an input. A temperature is then scanned or modulated. The response of the calorimeter is calculated. This predicts the sample thermocouple temperature and the temperature difference between the sample and reference thermocouples (ie counts) as a function of time and temperature. Using this operational mode it is possible to investigate the effects of sample size, heating rate and alloy composition. Non-equilibrium solidification effects and difficulty in nucleation can be included.

The numerical method is described and parameters for use in a Stanton Redcroft heat flux DSC, a TA Instruments DSC2010 and a Mettler Toledo DSC 821^e have been obtained. Examples of corrected experimental runs are given as well as predicted results with a multi-component alloy.

KEY WORDS: enthalpy measurements, heat capacity measurements, heat flux calorimeter; modulated DSC, numerical modeling.

1. INTRODUCTION

In a heat flux DSC, it is usually assumed that the temperature difference between the two pans or counts is proportional to the effective heat capacity difference between the sample and reference. This is not true when latent heat has just been evolved or absorbed [1,2]. In addition when significant heat is evolved the sample thermocouple does not measure the sample temperature and this leads to significant errors in apparent transition temperatures [1]. To reduce these problems DSC manufacturers usually recommend using very small samples. Unfortunately small samples lead to greatly reduced counts and loss of accuracy.

A numerical program has been written which models a heat flux calorimeter and allows the enthalpy and heat capacity 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 calculated as a function of the sample temperature.

In the second, temperature and temperature differences (counts) are predicted from a known variation of enthalpy against temperature. A thermodynamic package such as MTDATA [3] or a non-equilibrium solidification model such as ALLOY [4] can be used to give the enthalpy values.

2. 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 [5]. 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 [6]. A schematic diagram of the heat flux DSC is shown in Figure 1. The sample and reference are surrounded by a sample and reference container and are placed on the sample and reference plate. Typically in a heat flux calorimeter a thermocouple measures the sample plate temperature and another measures the difference in temperature between the sample and reference plates. Often the thermocouple output is not converted to a temperature difference and is referred to as counts. The plates and containers are placed in a uniform temperature enclosure.

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 be either by conduction or by radiation. That is the heat transfer between the different regions depends linearly on the temperature difference or on the fourth power of the two temperatures. The heat flux from the surroundings to the sample plate is assumed to be given by

$$q_{FP} = K_{FP}(T_F - T_{SP})$$

where K is a heat transfer coefficient. Similar heat fluxes occur between the sample plate and sample container

$$q_{PC} = K_{PC}(T_{SP} - T_{SC})$$

and between the container and sample (or reference)

$$q_{CS} = K_{CS}(T_{SC} - T_S).$$

The heat flux from the surrounding to the containers is assumed to be by radiation and the flux is:

$$q_{FC} = E_{FC}(T_F^4 - T_{SC}^4)$$

A final heat flux by radiation is assumed between the sample container and the reference container.

$$q_{SR} = E_{SR}(T_{SC}^4 - T_{RC}^4)$$

Similar fluxes can be defined for the reference side of the calorimeter.

A heat balance equation can be written for each of the six different regions of the calorimeter. In the present work the calculations are carried out 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 [7]. 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 heat capacity, T'_{SC} the container temperature at the start of the time step and ∂t is the time step. 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 method of solution is slightly different for the two different operational modes. 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.

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 versus 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.

The radiation fluxes can be made approximately linear by writing

$$q_{FC} = E_{FC}(T_F^4 - T_{SC}^4) = E_{FC}(T_F - T_{SC})(T_F + T_{SC})(T_F^2 + T_{SC}^2) = K_{FC}(T_F - T_{SC})$$

where K_{FC} is evaluated at the start of the time step.

Since all the equations could be made linear they were 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 was kept small so that thermal resistances could be estimated reasonably easily from experiment.

3. PROGRAM IMPLEMENTATION

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 a file. The procedure for obtaining this data is briefly discussed in appendix A. The sample mass and heat capacity of the pans and containers are entered. One of the two operational modes is then chosen.

4. 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 are used by the program to make a zero line correction [8]. 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. The results can then be plotted as a function of time or temperature. The results from pure Al heated/cooled at 10 K/min in a Stanton Redcourt calorimeter, Mettler Toledo DSC 821^e and TA Instruments DSC2010 are shown in Figure 3, 4 and 5. The sample size was 10 mg for the first 2 but 1.3 mg for the TA Instruments DSC2010. The calculated enthalpy is plotted against sample temperature as red lines. As expected, the latent heat appears as vertical line on the figures. The enthalpy line should be compared with the black lines on the enthalpy plot, which show the enthalpy that would be obtained by integrating the counts and plotting the results against sample thermocouple temperature. The corrected heat capacity plotted against sample temperature are shown by the red lines, and the black lines show temperature difference plotted against sample thermocouple temperature on the lower diagrams. The important 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 results

5. 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 in a Mettler calorimeter are shown in Figure 6. The sample temperature (red), sample plate temperature (green), surroundings temperature (blue) and the temperature difference (black) are plotted as a function of time, in Figure 6a The temperature difference (counts) is plotted against sample plate temperature in Figure 6b.

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 in a TA Instruments DSC2010. The red line show the enthalpy and heat capacity which were inputs and the black line on Figure 7b the calculated temperature difference (counts) that would be expected. The black line on

Figure 7a show the enthalpy that would be calculated by integrating the counts. From Figure 7b it can be seen that the temperature difference is not proportional to the heat capacity.

6. CONCLUSIONS

It is concluded that the program can give enthalpy and heat capacities from experimentally measured data. Insufficient trials have been carried to assess how reproducible the results will be for different samples and pans.

In the predictive mode it is clear that considerable information can be obtained by examining the effect of sample size and heating rate. Using the model it is easy to separate real kinetic effects in the sample from artifacts resulting from a over simplified analysis of a heat flux DSC.

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APPENDIX A. Setting calorimeter constants:

Values of the mass of the sample and the mass and heat capacity of the containers, plates, and reference are entered. The number of heat transfer coefficients are made small by assuming symmetry between the sample and reference side of the calorimeter. The emissivity term for radiation from the sample container to the reference container is taken to be the emissivity to the surroundings times the solid angle subtended by the sample over that for the surroundings. The calorimeter heat transfer coefficients are estimated 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.

At present there is no reliable way of setting E_{FC} . It is set to zero or at a value where the fraction of heat flow by radiation is just beginning to be significant at 600 C. The other 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 capacity in the solid and liquid are made correct by making small adjustments 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. It should be possible to use the values obtained for alloys with similar melting temperatures.

FIGURE CAPTIONS

Fig.1. A schematic diagram of a heat flux DSC showing the definition of the fluxes

Fig 2. The start up screen of the numerical model.

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

Fig 4. 10 mg pure Al sample heated/cooled at 10 K/min in a , Mettler Toledo DSC 821^e . a) calculated enthalpy (red line), enthalpy obtained by integrating counts (black line) and b) heat capacity (red line) and inputted temperature difference (black line).

Fig 5. 1.3 mg pure Al sample heated/cooled at 10 K/min in a TA Instruments DSC2010 . a) calculated enthalpy (red line), enthalpy obtained by integrating counts (black line) and b) heat capacity (red line) and inputted temperature difference (black line).

Fig. 6. Expected results for a 2 mg pure Al sample heated/cooled at 5 K/min. A nucleation supercooling of 5 K has been included. a) Predicted sample temperature (red), sample thermocouple (green), surroundings temperature (blue) and temperature difference (black) plotted against time. b) Predicted temperature difference plotted against temperature.

Fig. 7. The expected results for a 10mg sample of an alloy (LM25) heated at 4K/min in a TA instrument DSC2000. a) The inputted enthalpy (red) and predicted integrated counts (blue), b) The inputted heat capacity (red) and the calculated temperature difference (blue).

Figure 1

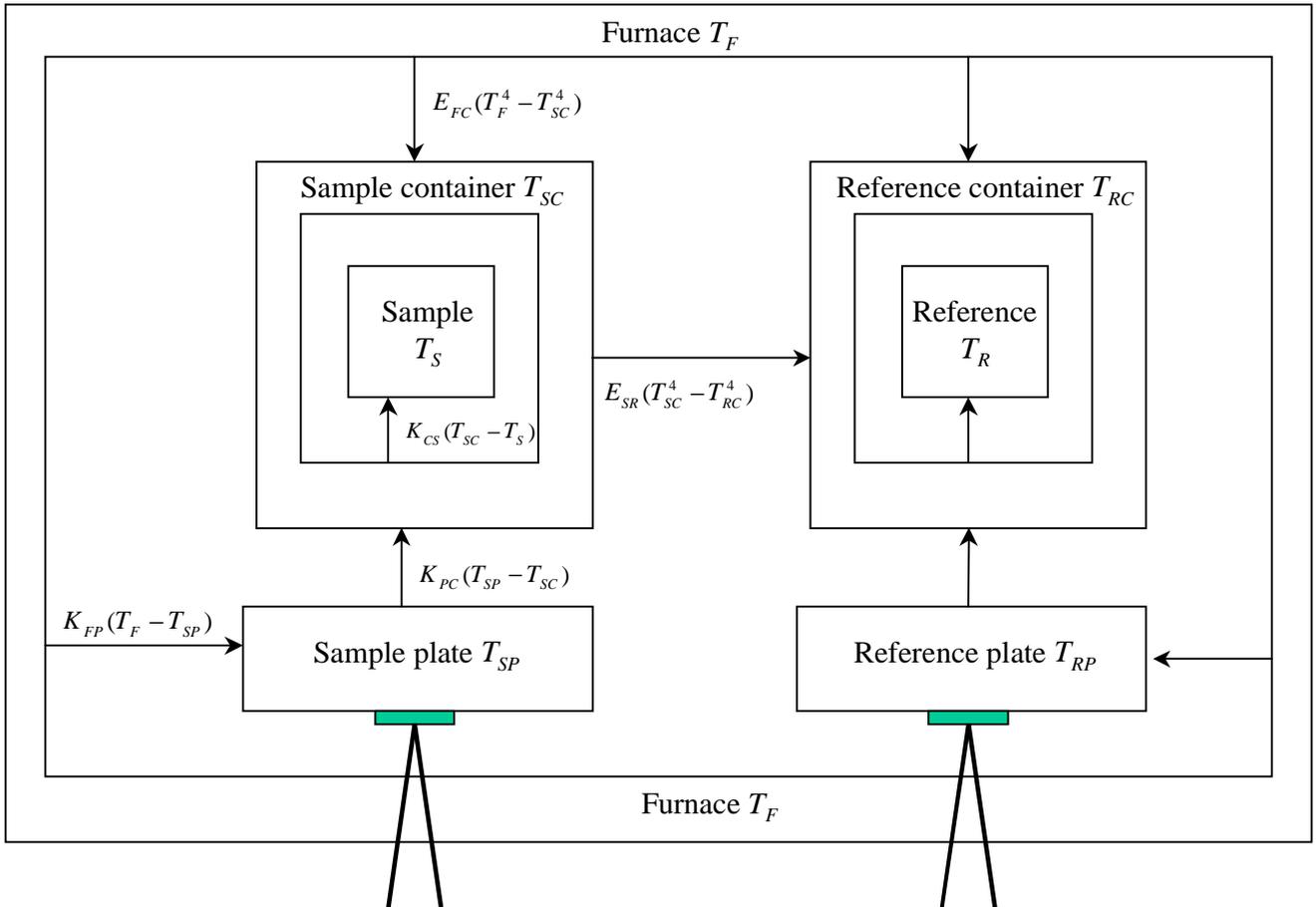


Figure 2

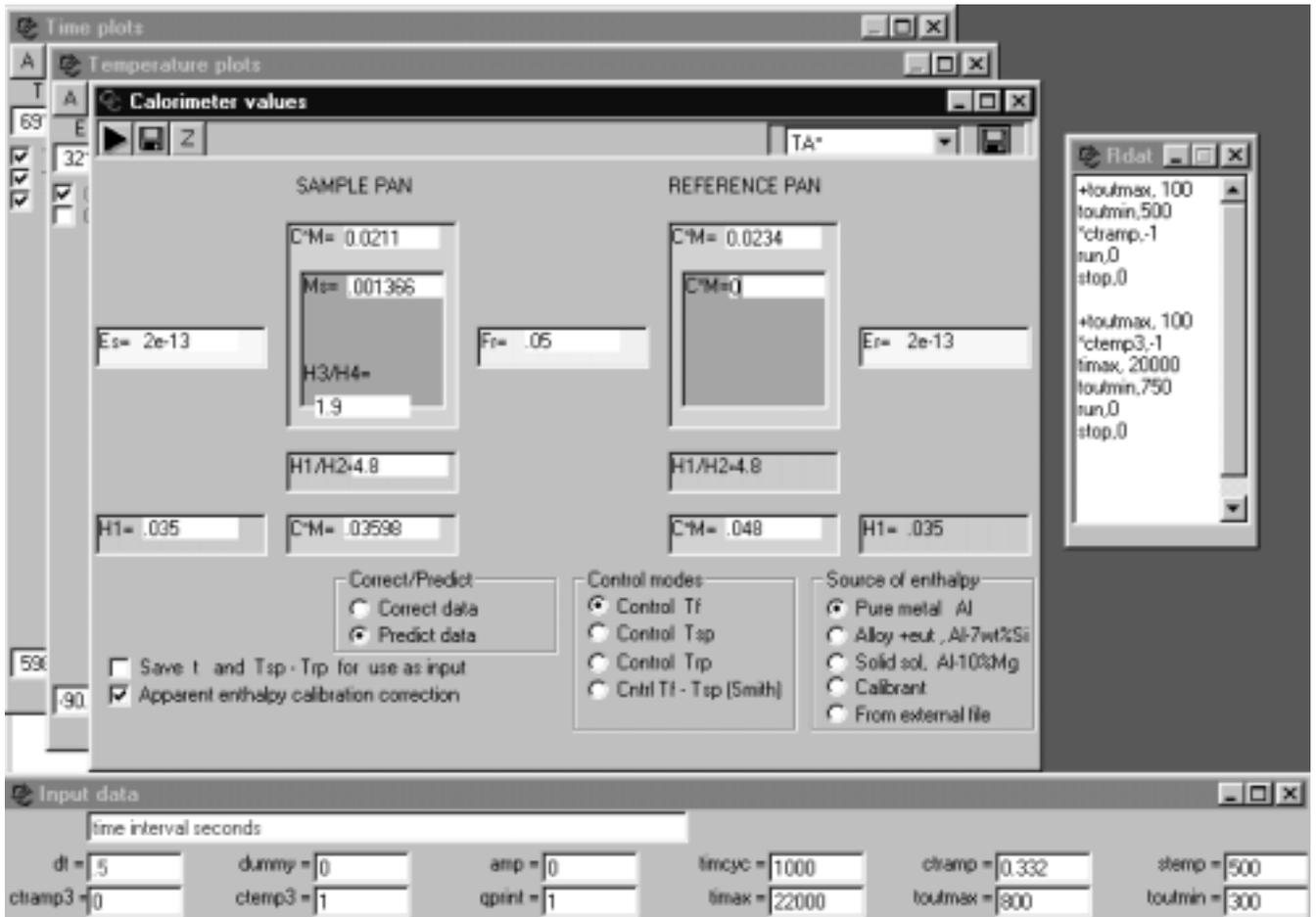


Figure 3

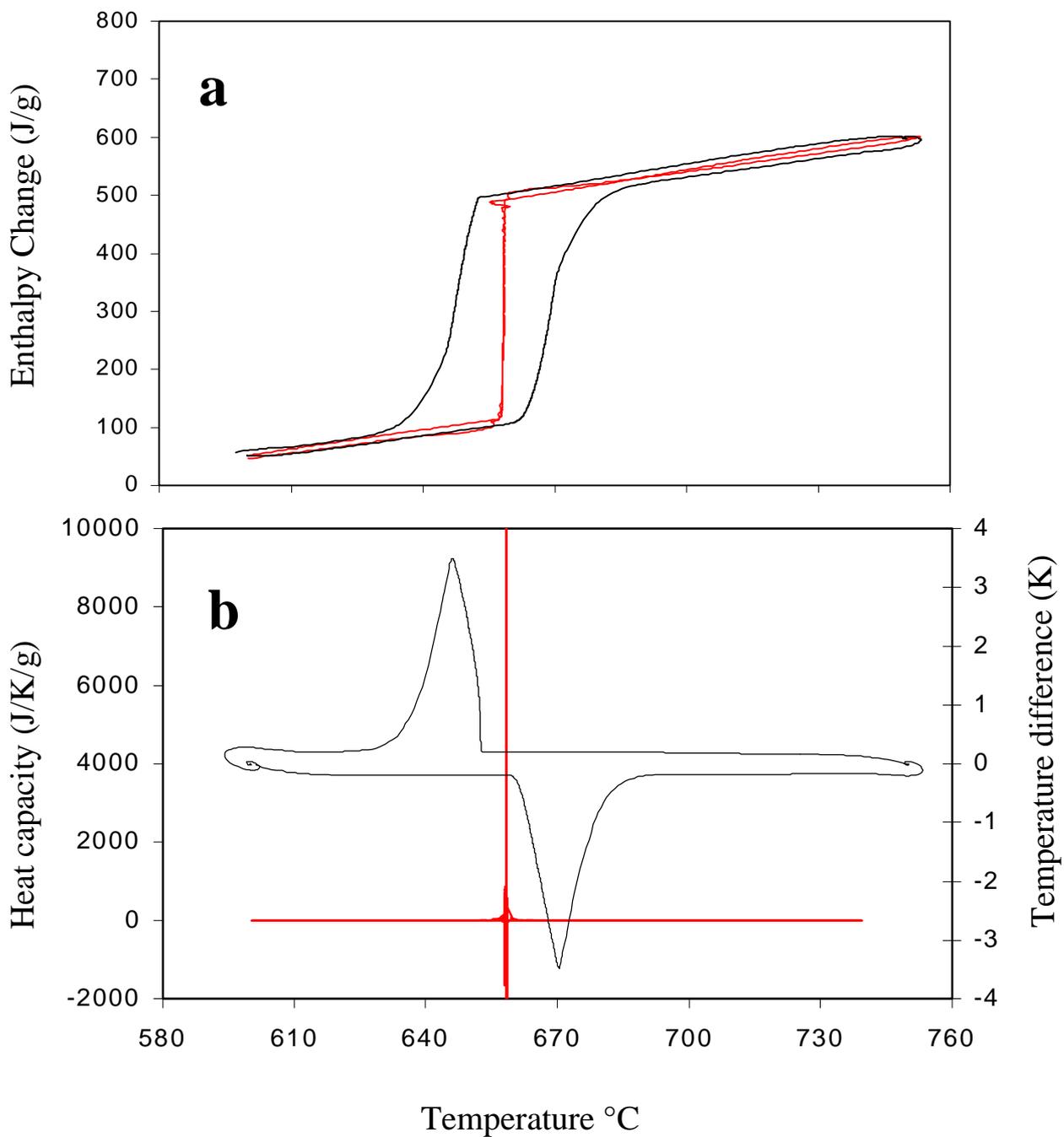


Figure 4.

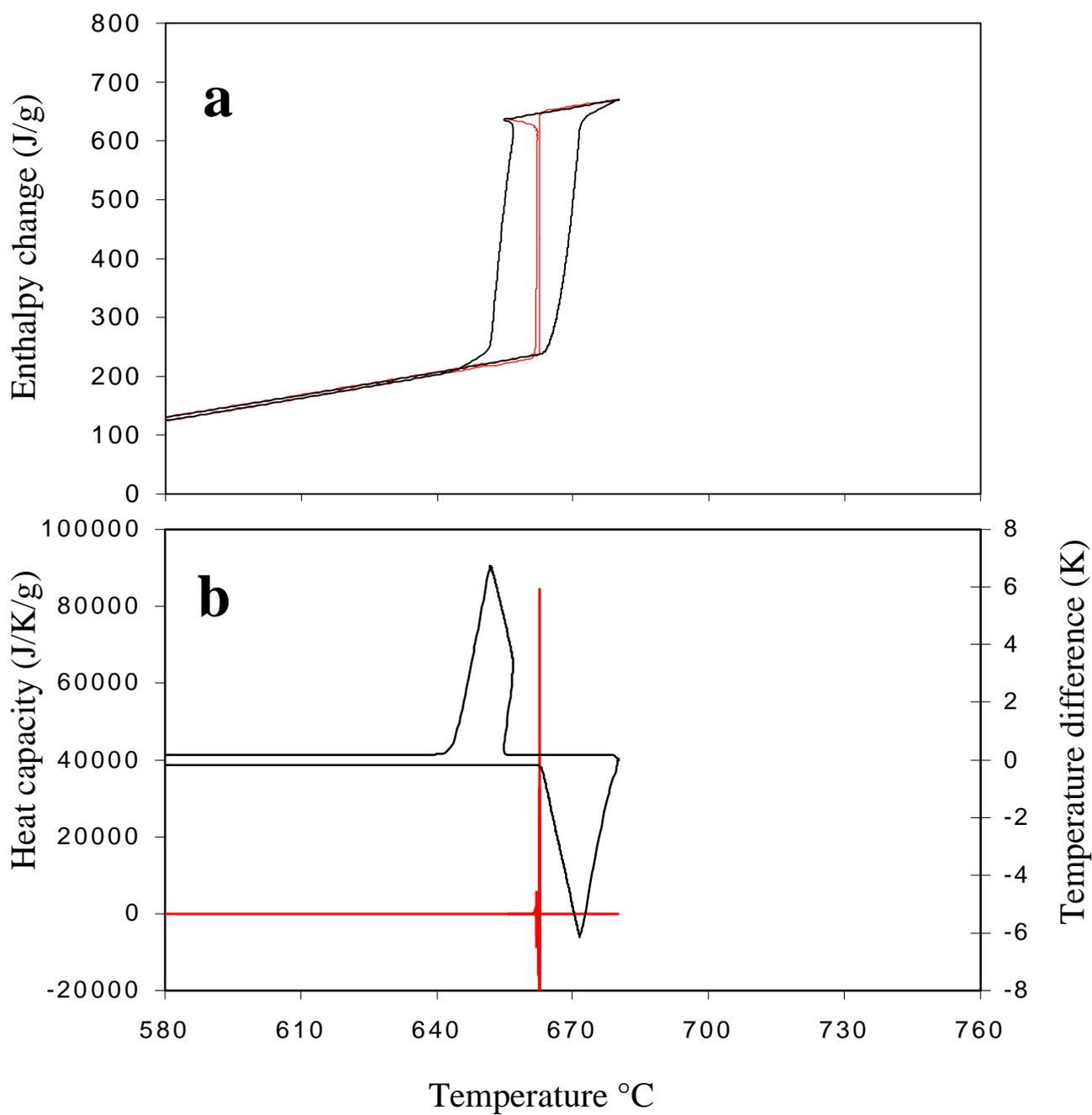


Figure 5

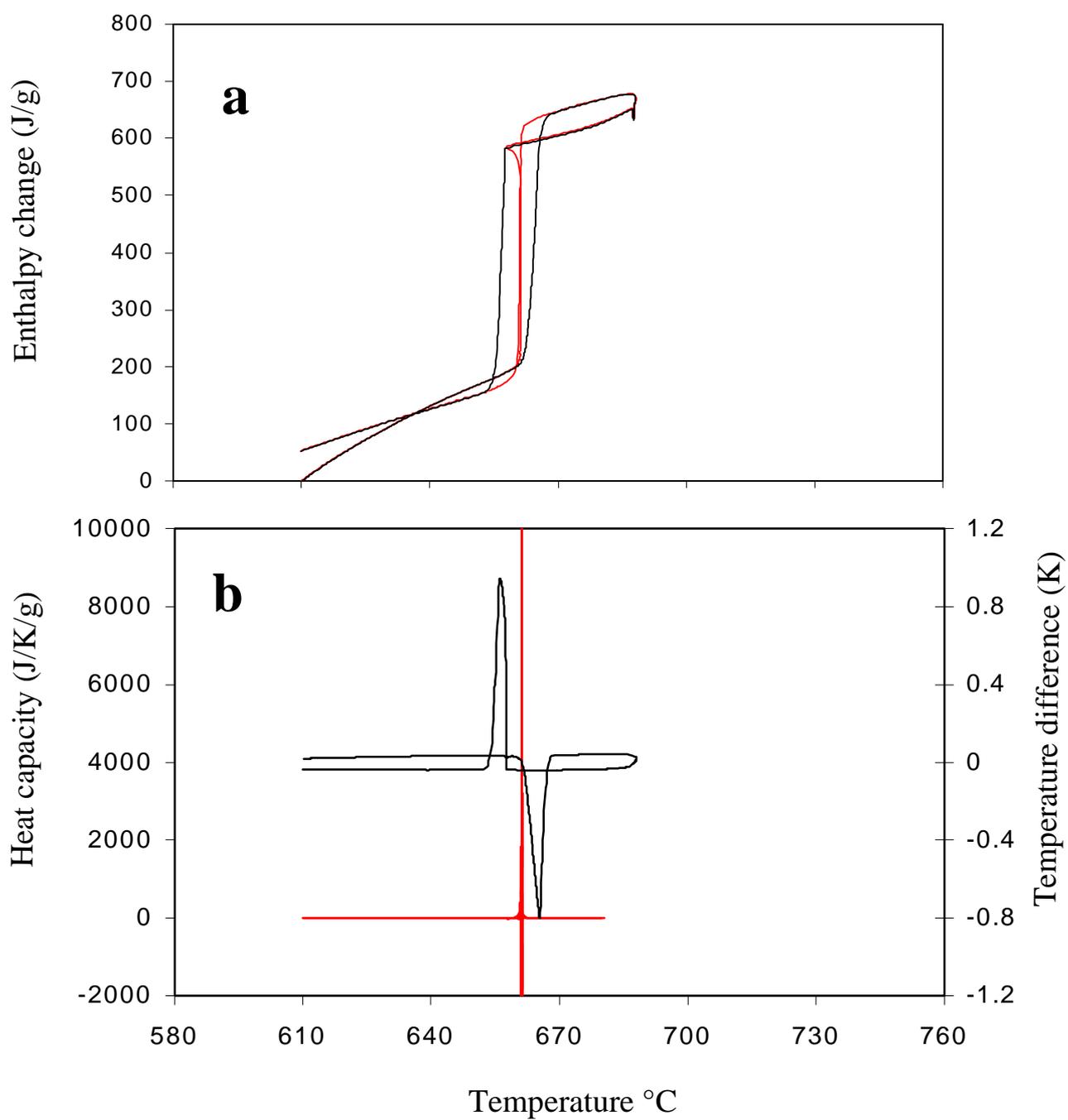


Figure 6

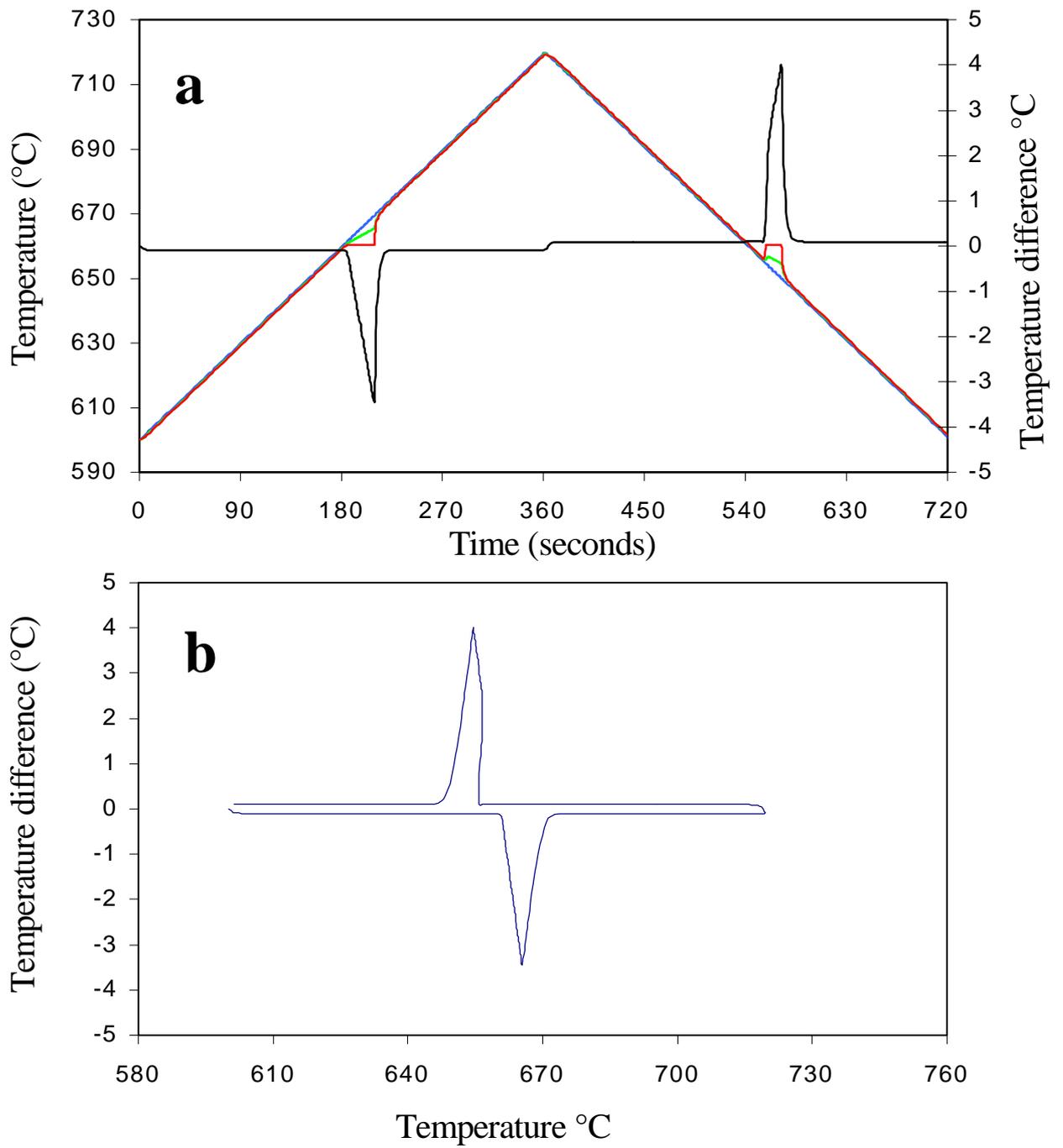


Figure 7

