Modification of the conventional measuring method to determine the specific heat capacity using a Perkin-Elmer DSC 2

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ABSTRACT

A description is given of a modified measuring and evaluation method to determine the specific heat capacity using a Perkin-Elmer DSC 2. Measurements are carried out with a sample and a calibration sample (sapphire) over the whole temperature range of interest, with starting and ending isothermals and several intermediate isothermals. The results of measurements on nickel carried out by this method are very well repeatable. The relative uncertainty is smaller than 3%.

Introduction

It has been the aim of our work to modify the method to determine the specific heat capacity using a Perkin-Elmer DSC 2 so that the time and effort to be spent and the relative uncertainty of measurement are reduced and the reproducibility improved.

To obtain good measurement results, a number of prerequisites must be met by both the classical and the modified method:

- The temperature of the sample holder surroundings must be constant. This can be achieved, for example, with a liquid nitrogen cooling device.

- The throughput of purge gas must remain constant.

- A transparent plastic dry box for mounting on the analyzer deck purged with nitrogen gas reduces the formation of condensate at low temperatures.

- Samples and crucibles must be prepared very carefully. The bearing surfaces of the crucibles and solid samples in particular must be plane to ensure good thermal contact.

- Crucibles and samples should be cleaned thoroughly for example in an ultrasonic bath.

- Recalibration of the DSC by means of calibration substances whose melting temperatures and enthalpies of fusion are known is necessary at two- to three-month intervals. The baseline must be checked daily with the crucibles empty and readjusted if necessary. A heating rate of 40 to 80 K/min can be chosen for this purpose.

- Short-time heating of the calorimeter prior to each measurement to a temperature at least 5 K above the maximum temperature of measurement applying a maximum heating rate of 160 K/min has proved its practical worth [1].

- The sample mass must be chosen so that the products of mass and specific heat capacity for sample and calibration sample (sapphire) are in as good agreement as possible.

Classical method

Large temperature ranges must be subdivided into smaller partial ranges so as to allow the starting and ending isothermals to be connected by straight lines for evaluation purposes. These partial ranges must overlap. In the case of the absolute method, a baseline and a sample curve are determined for each partial range, including starting and ending isothermals; in the ratio method, a curve of the calibration sample (sapphire) is determined in addition [2]. The samples must be exchanged several times for this purpose. The total time of measurement is additionally prolonged by the times elapsing until the isothermal state has been reached.

Modified method

The entire temperature range which is of interest here is traversed without interruption. A sample curve and a calibration sample curve (sapphire) including starting, ending and intermediate isothermals are measured.

The duration of the intermediate isothermals was varied between 1 minute and 5 minutes, resulting in that the $c_p(T)$ curves differ by 0.1% at most. We therefore normally use intermediate isothermals of 2 minutes. The spacing between two isothermals should

be 50 K to 100 K. Fig.1 is a schematic representation of the chronological development of a measurement. The program temperature has been plotted as a function of time: 1 constant initial temperature, 2 constant heating rate, 3 constant final temperature, 4 to 6 constant intermediate temperatures.
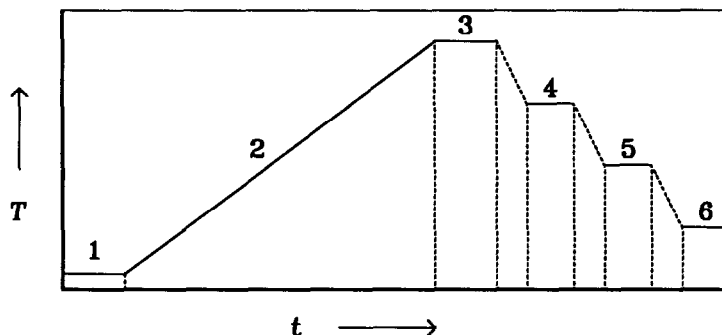

Figure 1. Program temperature T as a function of time t (1 initial isothermal, 2 scanning period, 3 final isothermal, 4 to 6 intermediate isothermals)
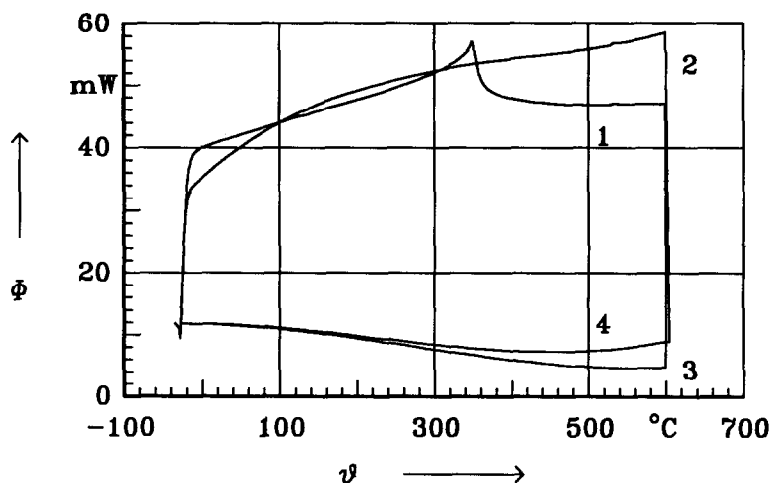

Figure 2. Heat flow rate ϕ measured for nickel (1), sapphire (2) and curves of the calculated isothermals for nickel (3) and sapphire (4) as a function of temperature ϑ, heating rate: 20 K/min.

In contrast to the classical method, in the method described here, the starting and ending isothermals are not connected by a straight line but by a polynomial of third order calculated from the end points of the measured isothermals. Fig.2 shows one curve each measured for nickel and sapphire, including the curves of the isothermals as a function of temperature.

Calculation of the specific heat capacity

In the equations below, the mass m is usually stated in g, the specific heat capacity c_p in J/(g·K), the DSC signal (heat flow rate ϕ) in W and the scanning rate β in K/s.

The meaning of the indices is as follows: s=sample, c=calibration material (sapphire), r=reference, cr=crucible, ϕ_s, ϕ_c, ϕ_B = differences (heat flow rate in the scanning mode minus heat flow rate in the isothermal mode) for sample, sapphire and unknown baseline (without crucibles).

The following is then valid for the sample measurement:

$$\phi_s - \phi_B = [m_s \cdot c_{p,s} + (m_{s,cr} - m_{r,cr}) \cdot c_{p,cr}] \cdot \beta \tag{1}$$

and for the pertaining measurement on sapphire:

$$\phi_c - \phi_B = [m_c \cdot c_{p,c} + (m_{c,cr} - m_{r,cr}) \cdot c_{p,cr}] \cdot \beta \tag{2}$$

where $c_{p,c}$ = specific heat capacity of the calibration material (sapphire) taken from the literature [3]

By combining the two equations, the following is obtained for the sample's specific heat capacity:

$$c_{p,s} = \frac{\phi_s - \phi_c}{m_s \cdot \beta} + \frac{m_c \cdot c_{p,c}}{m_s} + \frac{(m_{c,cr} - m_{s,cr}) \cdot c_{p,cr}}{m_s} \tag{3}$$

the assumption being that the same reference crucible is being used to measure the sample and the sapphire and the actual scanning rates are the same in both runs.

Sample temperature

In measurements in the heating-up mode, the sample temperature T_s is always lower than the program temperature $T_{ind.}$. At the transition to the final isothermal, an

additional heat flow rate, which decreases exponentially with time, is therefore needed to ensure that the sample temperature reaches the program temperature. The temperature difference $T_{ind.} - T_s$ can be calculated from the integral A of this heat flow rate over the time [4]:

$$T_{ind.} - T_s = \frac{A}{(m \cdot c_p)_{cr} + (m \cdot c_p)_s} \tag{4}$$

Fig. 4 shows the effect of this temperature correction on the results and the Curie temperature of nickel.

Measurement and evaluation

The temperature limits and the heating and cooling rates must be adjusted at the calorimeter. Control of the DSC and acquisition of the measured data are ensured by a personal computer (XT). The sample and segment parameters must be given in order that the measurement can proceed automatically.

A flexible evaluation program has been devised to represent and evaluate the data by different methods.

Results

Measurements of the specific heat capacity by the modified method described here have been carried out for about one year. The relative uncertainty of measurement is smaller than 3%.

The results of five measurements performed on nickel with a heating rate of 20 K/min are represented in Fig.3 and show a repeatability of 0.3 to 1% (dimensions of the nickel and sapphire samples: 6 mm in diameter, 1 mm in height). The values from the literature [5,6] are plotted for comparison. The deviation of the measured specific heat capacity from the literature values does not exceed 2%.

Two measurements on nickel at the heating rate of 20 K/min and the cooling rate of 20 K/min allow to demonstrate the difference between sample temperature and program temperature. Without temperature correction the Curie temperatures measured in the heating and cooling modes differ by 10 K. Temperature correction reduces this difference to 3.6 K. The results have been represented in Fig.4 without and with temperature correction as explained above.
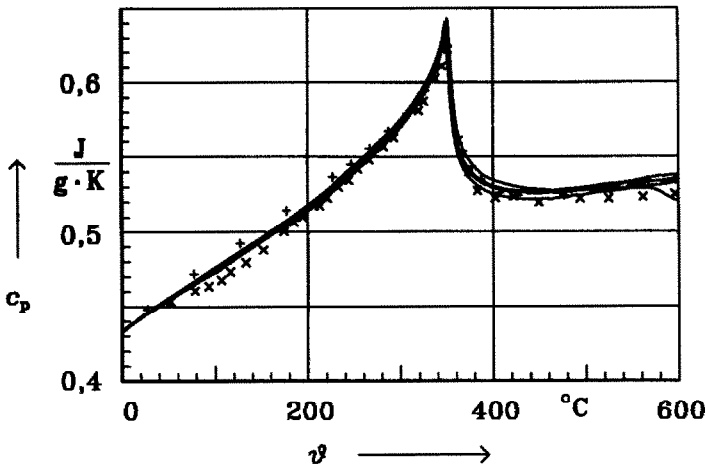
Figure 3. Specific heat capacity c_p of nickel as a function of the temperature ϑ (5 measurements at a heating rate of 20 K/min) and literature values (+ [5] and x [6])
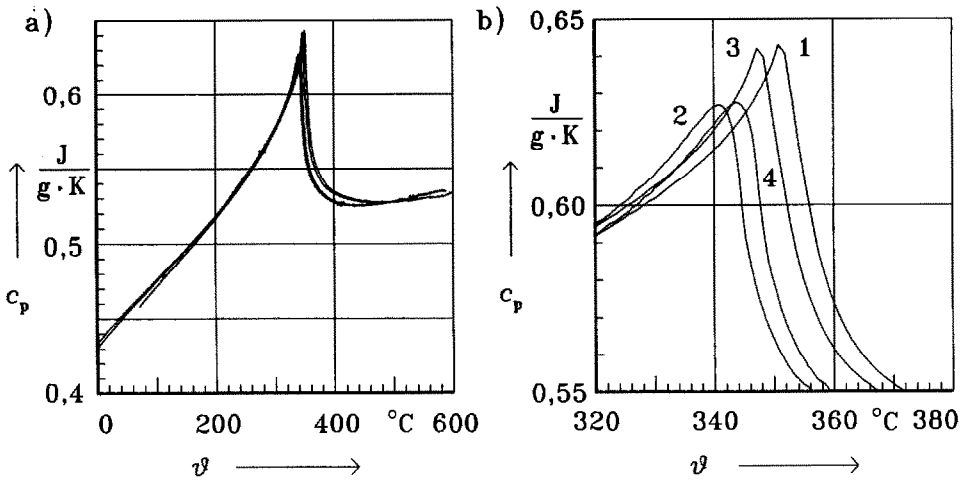

Figure 4.   Specific heat capacity c_p of nickel as a function of the temperature ϑ
a) entire temperature range b) around the maximum (Curie point)
(1) heating mode, (2) cooling mode without temperature correction, (3) heating mode,
(4) cooling mode with temperature correction, scanning rate: 20 K/min.

Repeatability of measurements at lower heating rates is not so good because the measuring signal becomes smaller and variations of the baseline can influence the results. When the measurements are performed at higher heating rates, the temperature gradients inside the sample are too great.

The results of measurements on other metals, alloys and ceramic materials are also well repeatable provided their structure does not change during heating or cooling.

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