Determination of heat capacity by temperature-modulated DSC at temperatures above 700 °C

The heat capacity of a material can be determined with high accuracy using temperature-modulated DSC. Measurements up to 700 °C can be performed by conventional DSC. In this article, we show how good results can also be obtained above 1000 °C using the TGA/DSC 1. To do this, we present ADSC measurements of nickel, sapphire and molybdenum in the temperature range 900 to 1400 °C. The work originated as part of an interlaboratory test organized in 2012/2013 by the Thermophysics Group of the German Society for Thermal Analysis (Gefta).

Introduction

Several different procedures for determining the specific heat capacity by DSC are available, such as for example the sapphire method [1, 2]. The maximum temperature of the DSC is however 700 °C. The article in reference [3] describes how specific heat capacities can be determined using the sapphire method up to a temperature of 1400 °C with an accuracy of about 10%. Application examples are presented in reference [4].

When the TGA/DSC is used to determine specific heat capacity, the heat flow signal measured simultaneously with the TGA signal is evaluated just as in DSC measurements. Other DSC methods that are available include the temperature-modulated techniques IsoStep® [5], Steady-State [3], ADSC [6] and TOPEM® [7, 8]. TOPEM® is currently not implemented for TGA/DSC.

Compared with the sapphire method, temperature-modulated methods have the advantage that they are less affected by drift and can therefore achieve accuracies of up to 2%. Heat capacities can also be determined for isothermal conditions using Steady-State, ADSC and TOPEM®.

In addition, information is obtained about the contributions of sensible and latent heat capacity. However, these methods require considerably longer measurement times compared with the sapphire method. In this article, we present specific heat capacity measurements determined by ADSC in the temperature range 900 to 1400 °C. The measurements were performed using the TGA/DSC 1.

ADSC method

The temperature-time program T(t) of an ADSC measurement is a function consisting of a constant heating rate \( \beta_0 \) overlaid with a sinusoidal component: \( T(t) = \beta_0 t + T_A \sin(\omega t) \) with a temperature amplitude \( T_A \) and a frequency \( \omega = 2\pi/p \) (with a period \( p \)).

The time-dependent heating rate \( \beta(t) \) is given by \( \beta(t) = \beta_0 + \beta_A \cos(\omega t) \) with the heating rate amplitude \( \beta_A = T_A \omega \).

The period \( p \) must be considerably larger than the thermal lag of the furnace. Our measurements were performed using a TGA/DSC 1 equipped with a high-temperature furnace and the so-called DTA sensor. The time constant of this is about 100 s. The period should be in the range 5 to 10 min.
The heat capacity corresponds to the contribution of the complex heat capacity, which is calculated from the ratio of the amplitude of the heat flow and the heating rate. The calibration factor is determined from measurements using a reference material of known specific heat capacity.

Normally sapphire is used as the reference material. In addition, we have also used molybdenum from NIST (National Institute of Standards and Technology) in order to have another material of a known specific heat capacity.

Measurements and results

General comments

To determine the specific heat capacity by ADSC, three measurements have to be performed under identical conditions, namely measurement of the sample, measurement of the reference substance, and measurement of the empty crucible for the determination of the blank curve. A practical working procedure is:

- Measurement with empty crucibles,
- Sample measurement,
- Measurement of the reference material,
- Measurement with empty crucibles.

The first measurement with the empty crucibles is not used for the evaluation. The curves of the sample and reference material are corrected using the second blank measurement. The ADSC evaluation then yields the uncorrected complex specific heat capacity $c_{p,sample}^{uncorr}$.

This must be corrected with the measured complex specific heat capacity of the reference material $c_{p,ref}^{uncorr}$ and its literature values $c_{p,ref}^{lit}$. To do this, the literature values $c_{p,ref}^{lit}$ are stored as a curve by the STAR® software. The STAR® software then calculates the specific heat capacity curve of the sample from the three other curves according to the equation $c_{p,sample} = c_{p,sample}^{uncorr} / c_{p,ref}^{uncorr} \times c_{p,ref}^{lit}$.

The ADSC measurements presented here were performed for nickel, molybdenum and sapphire using 30-μL platinum crucibles. The sample and reference crucibles were identical for all measurements. The underlying heating rate was 1.5 K/min, the temperature amplitude 5 K and the period 6 min. The measurements were performed in the temperature range 900 to 1400 °C. The blank curve subtracted heat flow curves are displayed in Figure 1.

Measurement of nickel and molybdenum using sapphire as reference material

First, let us look at the results of the measurements of the specific heat capacities of nickel and molybdenum (Figure 2). The sapphire measurement is used as the reference measurement. The literature values for nickel [9] and molybdenum [10] are given in addition. The curves of the specific heat capacities for molybdenum are within 2% of the literature values. The deviation for nickel is about 5%.

Measurement of nickel and sapphire using molybdenum as reference material

Instead of sapphire, we now want to use molybdenum as the reference material. Figure 3 displays the results for nickel and sapphire together with the literature data as well as the curves for deviations of 2% and 5%. The results for nickel are independent of the reference substance used.

Summary

Using ADSC, the specific heat capacity of sapphire and molybdenum could be determined with an accuracy of 2%. For nickel, the deviation from the literature values was 5%. The literature values were determined using a pulse calorimeter with an accuracy of 2%. The additional deviation can possibly be explained by the nickel alloy having a slightly different composition. Since the Curie temperature is sensitive to the composition of the alloy, the Curie temperature determined using TOPEM® measurements should be given for comparison: $T_c = 358.2$ °C. This value is 1.6 K less than the value of $T_c = 359.85$ °C given by Meschter [9] and could therefore explain the somewhat different results.
higher deviation of 5% compared with deviations of only 2% for the sapphire and molybdenum measurements.

- Make sure the instrument has been switched on long enough before beginning the measurement and that the purge gas flow is stable.
- If possible, the same crucible should be used for the blank, sample, and reference measurements. Possible differences in mass when using different crucibles should be taken into account in the calculation of the heat capacity.
- Aluminum crucibles cannot be used because of the high temperatures. Crucibles made of platinum can be used instead. They exhibit good thermal conductivity. Crucibles with volumes of 30, 70, and 150 µL are available. The size of the crucible should be as small as possible. To minimize heat losses, the crucibles are used with a lid.
- If the TGA/DSC is equipped with the platinum sensor, there is the risk that the platinum crucible sticks to the sensor at high temperatures. This can be prevented by placing a sapphire disk between the sensor and the crucible.
- Likewise, at high temperatures, the platinum crucible can stick to the platinum lid. This can be prevented by using a ceramic paste (e.g. Ceramabond), which is applied to the rim of the lid.
- The mass of the sample, \( m_s \), and the mass of the reference substance, \( m_{\text{ref}} \), should be chosen so that the heat capacities are about the same:
  \[
  C_p,\text{sample} = m_{\text{sample}} \times C_p,\text{sample} \approx m_{\text{ref}} \times C_p,\text{ref} = C_p,\text{ref}.
  \]
- The crucibles should be precisely positioned on the sensor.

**Conclusions**

Temperature-modulated measurements using the heat flow signal measured simultaneously with the TGA signal by the TGA/DSC 1 can be used to determine heat capacities in the same way as in DSC measurements. This allows you to benefit from the advantages that temperature-modulated procedures offer compared...
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with the sapphire method when using the TGA/DSC. The advantages include the elimination of drift, the separation of sensible and latent heat capacity, and the possibility of determining isothermal heat capacities.

It was shown that the heat capacity can be determined with an accuracy of better than 5% for temperatures above 1000 °C.

References

Publishing Note:
This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 39.
See www.mt.com/ta-usercoms