Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 385–391

ACCURATE MEASUREMENT OF TRANSFORMATION ENERGETICS AND SPECIFIC HEAT BY DSC IN THE HIGH-TEMPERATURE REGION

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Abstract

A new differential scanning calorimeter NETZSCH model DSC 404 C Pegasus was developed for the measurement of specific heat and transformation energetics. The system allows tests between –120 and 1650°C with high accuracy. Presented in this work are the design of the DSC and measurements on various kinds of materials such as ceramics and metals, demonstrating the capability of the new system at low temperatures as well as in the high-temperature region.

Keywords: differential scanning calorimetry, enthalpies, specific heat, transition temperatures

Introduction

Knowledge of the thermophysical properties such as specific heat is becoming more and more important in the field of research and development of new products and materials. For an increasing number of applications these properties have to be known over a wide temperature range, especially at high temperatures. For example, the results of finite element and finite difference simulations for analysis of heat transfer problems strongly depend on the accurate knowledge of these thermophysical properties. Differential scanning calorimetry (DSC) has been used for decades for the characterization of caloric effects of various kinds of samples. This technique allows characterization of transformation energetics as well as measurement of the specific heat. However, due to problems resulting from the increasing radiative heat transfer at high temperatures, most instruments are not suitable for accurate tests above ≈700°C. Only a few instruments are commercially available up to temperatures of 1500°C [1]. The new DSC 404 C Pegasus® is designed for temperatures up to 1650°C, easy handling and improved performance. A new innovative user-exchangeable DSC-c_p-sensor was developed allowing measurements with stable baselines and optimized signal-to-noise ratio even at temperatures above 1500°C.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The schematic design of the high-temperature differential scanning calorimeter is depicted in Fig. 1. The furnace is mounted on a motorized hoist allowing reproducible placement of the furnace in the system. The furnaces are user exchangeable. For subambient temperatures a furnace with an integrated cooling coil can be employed. Connection of a liquid nitrogen cooling device allows measurements between –120 and 750°C. For temperatures up to 1650°C, another furnace with rhodium heating elements can be employed. The special design of the heating elements in the furnaces allows homogeneous heating of the sensor head over the entire temperature range. Homogeneous heat flow from the tube furnace to the sensor is crucial for a stable baseline. The DSC 404 C can be equipped with various sensor types to optimize the system regarding temperature range, atmosphere, sensitivity and time constant depending on the required application. The user-exchangeable sensors are fixed in a micrometer adjustment system. The adjustment system allows positioning and centering of the sensor head in the furnace and therefore fast optimization of the baseline. A new metallic DSC-c_p plate-type sensor was developed for accurate specific heat measurements at high temperatures. The new heat flux sensor is easy to handle and yields outstanding baseline stability and reproducibility over the entire temperature range. This allows, together with the high sensitivity and optimized signal-noise ratio, determination of specific heat with an uncertainty of ±2.5% for most materials. Due to the vacuum-tight construction of the cell, measurements are possible on samples sensitive to oxidation.

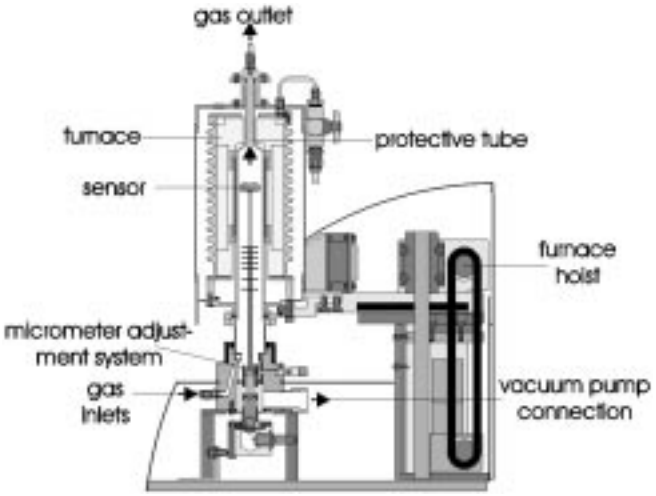

Fig. 1 DSC 404 C Pegasus, 1650°C-Version

Determination of the specific heat was carried out employing the ratio method [2]. Using this method three measurements under the same test conditions are neces-

sary. The first one is a measurement with empty crucibles, the baseline run. The measured signal can be described by the following equation:

$$V_B(T)=C(T)A(T) \tag{1}$$

$V_B(T)$ is the measured difference in thermocouple voltages between sample and reference, $C(T)$ is a correlation factor (including heating rate and sensor sensitivity) and $A(T)$ is the influence of the crucibles.

In the second measurement a standard material of known specific heat is employed in the sample crucible. The standard material is in most cases monocrystalline alumina (synthetic sapphire). The signal measured during this calibration run can be described by Eq. (2).

$$V_{cal.}(T)=C(T)(A(T)+m_{cal.}\,c_{p,cal.}(T)) \tag{2}$$

In this equation $m_{cal.}$ and $c_{p,\,cal.}(T)$ are the mass and the specific heat respectively, of the standard material employed for the test.

In the third run the sample being analyzed is put into the sample crucible. The resulting measurement signal can be described by Eq. (3):

$$V_{sam.}(T)=C(T)(A(T)+m_{sam.}\,c_{p,sam.}(T)) \tag{3}$$

Here, $m_{sam.}$ and $c_{p,\,sam.}(T)$ are the mass and the specific heat respectively, of the sample. Using the masses of the standard material and the sample and the specific heat of the standard material, calculation of the specific heat is possible by combining Eqs (1), (2) and (3). This yields:

$$c_{p,sam.}(T)=\frac{m_{cal.}}{m_{sam.}}\frac{(V_{sam.}(T)-V_B(T))}{(V_{cal.}(T)-V_B(T))}c_{p,cal.}(T) \tag{4}$$

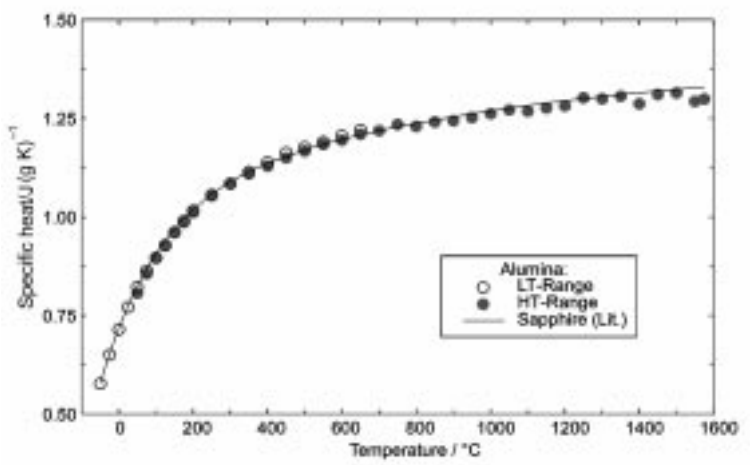

Fig. 2 Specific heat of α-alumina between –50 and 1600°C. Additionally shown are the literature values [3] for monocrystalline alumina (sapphire)

Results and discussion

Different materials such as ceramics, inorganics and metals were tested in the DSC to check the reproducibility and accuracy of the system for the various applications. Generally, the tests were carried out at heating/cooling rates of ≈20 K min^{-1} under defined atmospheres. In Fig. 2 the specific heat of polycrystalline α-alumina is depicted between –50 and 1600°C. Additionally, the literature values for pure monocrystalline alumina (synthetic sapphire [3]) are shown. The measurements were carried out employing two different furnaces on the same base unit. Platinum crucibles with lids were used for the tests. An inert atmosphere was employed. A good agreement was achieved between low- and high-temperature results. The deviations between the test results and literature values are generally less than 2.5% over the entire temperature range.

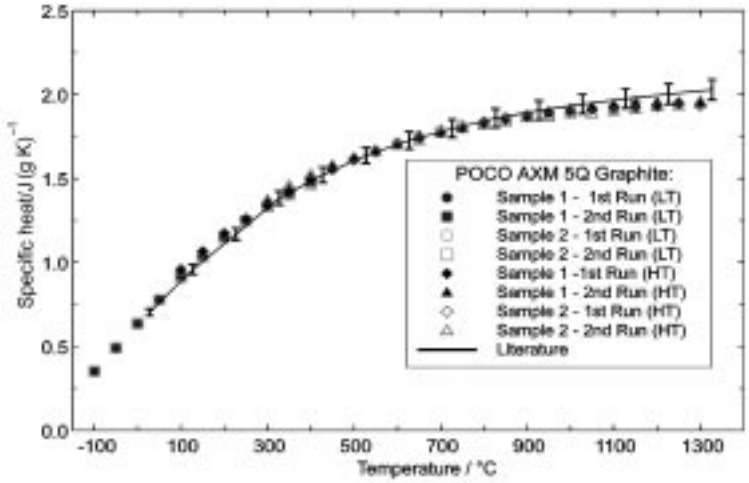

Fig. 3 Specific heat of POCO AXM 5Q graphite between –100 and 1300°C. Additionally shown are literature values for a similar material

The specific heat results measured on POCO AXM 5Q graphite are presented in Fig. 3. Measurements were carried out employing a low-temperature furnace between –100 and 400°C. Two different samples were tested twice. Two further samples were measured twice between 100 and 1300°C using a high-temperature furnace. In order to avoid oxidation pure inert atmospheres were employed for all tests. The literature values [4] for POCO AXM 5Q1 graphite are additionally shown in the figure. It can be clearly seen that the deviation between the individual measurement results is generally less than ±2%. Compared to literature values a good agreement was achieved at low-temperatures. At higher temperatures slightly lower values were obtained compared to literature. However, the results still agree within the accuracy

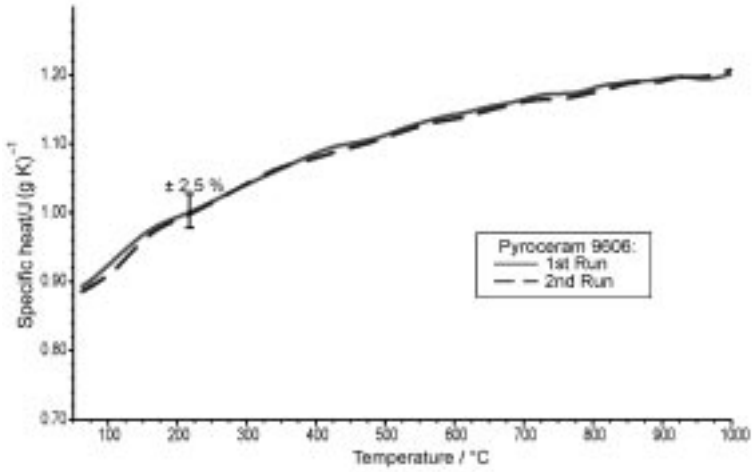

Fig. 4 Specific heat of Pyroceram 9606 between 50 and 1000°C. (Two runs on the same sample)

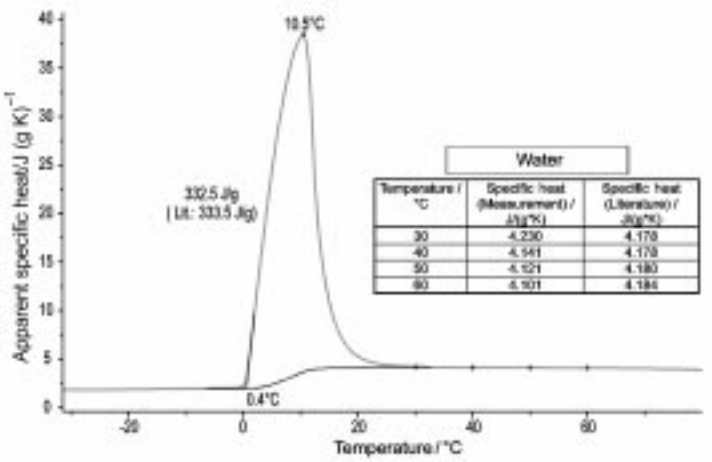

Fig. 5 Apparent specific heat of water between ≈ –35 and 80°C. Included is a table with a comparison of the specific heat with literature values [6]

of the instrument and the uncertainty of the literature values. Of course, the differences can be due to the different samples tested, as well.

In Fig. 4 the specific heat of Pyroceram 9606 is presented between 50 and 1000°C. The same sample was measured twice. The measurements were carried out in argon using platinum crucibles with lids. A good reproducibility (generally better than 2%) was achieved over the entire temperature range. The deviations compared to literature values [5] were generally less than ±2%.

Figure 5 shows the apparent specific heat of water between ≈ –35 and 80°C. The measurements were carried out in a helium atmosphere. Aluminum crucibles with

lids were used. The lids and crucibles were cold welded prior to the test. Therefore, a closed system was formed, avoiding evaporation of the water in the dry purge gas. In the measured result it is clearly visible that the apparent specific heat strongly increases during melting. The melting point was detected at 0°C. The heat of fusion 332.5 J g^{-1}. Melting temperature as well as heat of fusion are close to the literature value for water [6]. The heat of fusion overlaps the specific heat between 0 and ≈30°C. The difference of the measured specific heat between 30 and 60°C compared to literature values [6] is generally less than 2%.

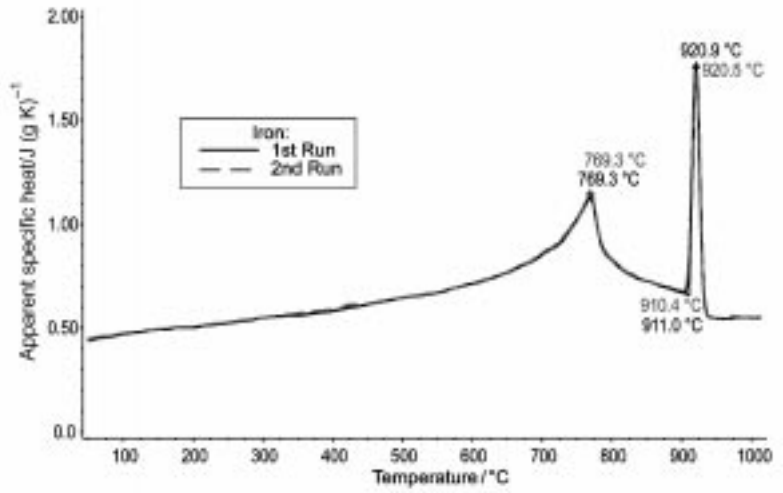

Fig. 6 Apparent specific heat of iron between 50 and 1025°C. The sample was measured twice

Figure 6 depicts the apparent specific heat of iron between 50 and 1025°C. The same sample was measured twice. The measurements were carried out employing platinum crucibles with lids. The atmosphere was pure argon. The heating rate employed here, was 4 K min^{-1}. After the test no surface oxidation was visible on the sample. Again, a good repeatability of the measurement results was achieved. At ≈769°C (peak temperature) the Curie transition was detected. The material changes from ferromagnetic to paramagnetic. At ≈910°C the extrapolated onset temperature of a change in the lattice structure (body-centered cubic to face-centered cubic) was measured. The results for the transition temperatures are in excellent agreement with the literature values for pure iron [6].

In Fig. 7 the apparent specific heat of a partially amorphous Ti60Cr40-alloy is shown between room temperature and 1500°C. Titanium alloys are well-known for being extremely sensitive to oxygen at elevated temperatures. The alloy was measured using platinum crucibles with alumina liners and lids. The inner surface of the crucibles was coated with an yttria spray to avoid reaction between the titanium alloy and the alumina liner. For the tests the DSC was evacuated with a turbo molecular pump system several times and backfilled with a pure argon atmosphere. During heating an exothermal effect

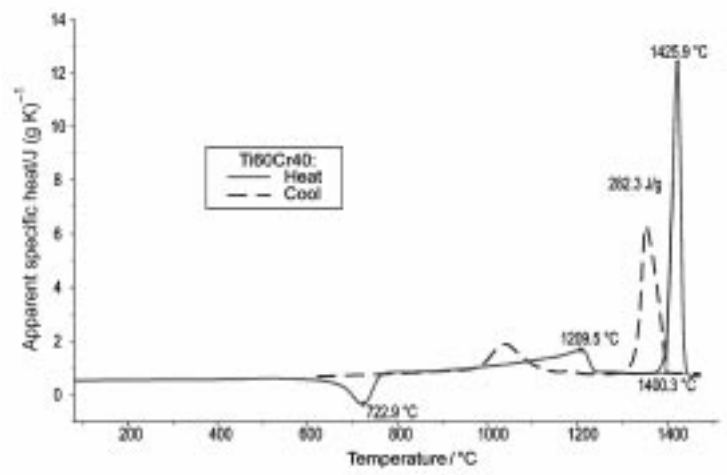

Fig. 7 Apparent specific heat of partially amorphous Ti60Cr40 between room temperature and 1500°C (heat and cool)

was detected in the apparent specific heat at 723°C (peak temperature). This effect is due to cold crystallization of the partially amorphous sample. Between ≈900 and ≈1250°C a phase transition was detected. Melting of the sample was measured at 1400°C (extrapolated onset). The heat of fusion was 282.3 J g^{-1}. In the liquid region the measured specific heat on heating was slightly lower compared to the cooling run. This is most probably due to a surface reaction between the alloy and the yttria coating and a change in the sample geometry. Outside the transition ranges a good agreement was achieved between heating and cooling run.

Conclusions

A new high-temperature differential scanning calorimeter was developed for measurement of specific heat and transformation energetics between –120 and 1650°C. Measurements on various kinds of materials clearly demonstrate the capability of the system. The possibility of measurements under very pure atmospheres allows, for example, measurements on materials sensitive to oxidation.

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