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Selection of an optimum calorimetry method for measuring specific heat of ceramics at high temperature [a]

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Abstract

The needs for accurate specific heat data on ceramics at high temperature are increasing greatly in many fields. The calorimetric techniques, and especially differential scanning calorimetry, are largely used for the determination of specific heat of materials. However, the precision of the measurement largely varies with the type of calorimetric detector, and also most of the calorimeters have a range of temperature limited below 1000 °C. In order to give access to specific heat of solids at high temperature with a good accuracy, a new high temperature calorimeter has been developed, around two different detectors: the heat flux DSC detector and the drop calorimetric detector. The different methods of specific heat determination (continuous heating, step heating, sample drop) are used with the new multi-detector high temperature calorimeter.

INTRODUCTION

The needs for accurate specific heat data on ceramics at high temperature are increasing greatly in many fields. Specific heat is an important thermodynamic parameter. Combined with thermal conductivity, it enables evaluation of the thermal diffusivity of materials.

To measure specific heat, many different techniques are available and the calorimetric methods, adiabatic, isoperibolic, heatflux calorimetry, drop calorimetry, modulation or levitation calorimetry, are very well adapted for such determinations [1]. Differential scanning calorimetry (DSC) has provided an easy determination of specific heat values [2].

With data processing computers, experimentation is easy and fast to run. However, the accuracy obtained for the data is largely dependent on the type of DSC detector used for the measurement. The detectors based on a transducer surrounding the sample completely give the best accuracy, according to either the continuous heating method or the step heating method [3–5]. An accuracy better than ±1% is easily reached.

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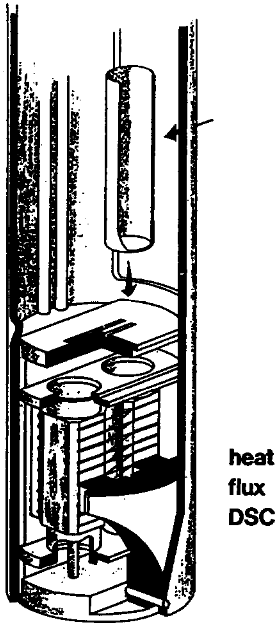

Fig. 1. Heatflux DSC detector.

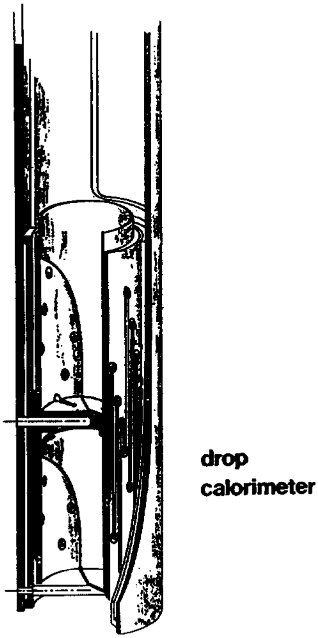

Fig. 2. Drop calorimeter.

However, these types of DSC are limited by their range of temperature, the maximal temperature remaining below 1000 ° C. Above this temperature, drop calorimetry is used to measure specific heat. In this case, the accuracy is not as good as previously, but remains lower than 5% [6].

However, today there is an increasing demand for measuring specific heat at high or very high temperature, especially in the field of oxide ceramics and engineering ceramics. In order to increase the possibilities of measuring specific heat towards high temperatures, a new surrounding heat flux differential scanning calorimeter has been designed, operating up to 1600 ° C. In the same time, a new calorimetric detector, having a large volume container, has been designed for the sample drop technique.

The new high temperature calorimeter, with the two detectors, gives a choice of specific heat determinations (continuous heating mode, step heating mode, sample drop technique) for all types of ceramics up to very high temperatures.

HEAT FLUX DSC DETECTOR

The heatflux DSC detector (Fig. 1) is built of two container holders set vertically side by side, and linked through two conductive sheets. They hold the differential detectors made of a set of thermocouples (20), the junctions of which are in series with the other container holder. A cross strut and mounting clips are used to limit the space around the container holders. No cement is used for fixing in order to facilitate the mounting and dismounting of the detector. The detector is set in a cylindrical enclosure supported by a tube bearing the wire connections.

In such a detector, the sample located in the container is completely surrounded by the transducer. This situation is unlike that in plate DSC detectors, in which only the bottom of the container is in contact with the detective sensor.

This design is especially interesting for measuring specific heat of solid materials, such as ceramics, because it is necessary to integrate the total heat exchanged by the sample when it is heated.

The heat flux DSC detector has an available volume equal to 0.45 cm^3 for sampling testing up to 1400 or 1600 °C according to the type of thermocouples used for the detector.

DROP CALORIMETRIC DETECTOR

Drop high temperature calorimetry is used in many laboratories for different types of applications, for example, heat of dilution, heat of formation, and specific heat [7]. However, the performance of the detector is limited by the crown type sensor used in this model. Its sensitivity varies with the sample filling [8]. In order to limit this variation, some improvements have been tried, especially setting the junctions of thermocouples at two different levels [9] or distributing the weldings on the total surface of the experimental chambers at different heights [10].

This last principle has been used to design a new drop calorimetric detector (Fig. 2). Two containers, with different sizes, are set one above the other. The lower container, the "reference", is intended to contain a thermally inert reference material, in order to compensate the heat capacity of the sample located in the upper container.

The two containers are located in a ceramic tube. On the wall of this tube, 52 vertical grooves have been machined, to receive the thermopile of 28 + 28 thermocouples connected in series. The thermopile covers the total surface of measurement and reference containers. One of the thermocouples is located under the base of the container. The thermopile is protected by a ceramic sleeve, and the detector is supported by a tube bearing the wire connections.

The container volume (6.2 cm^3) is larger than that of the differential scanning calorimeter. The drop calorimetric detector is used at constant temperature or with temperature scanning up to 1300 or 1500 °C according to the type of thermocouples used for the detector.

DETERMINATION OF SPECIFIC HEAT

The new multidetector high temperature calorimeter is used for measuring specific heat of solid materials according to three different methods, continuous heating, step heating and sample drop.

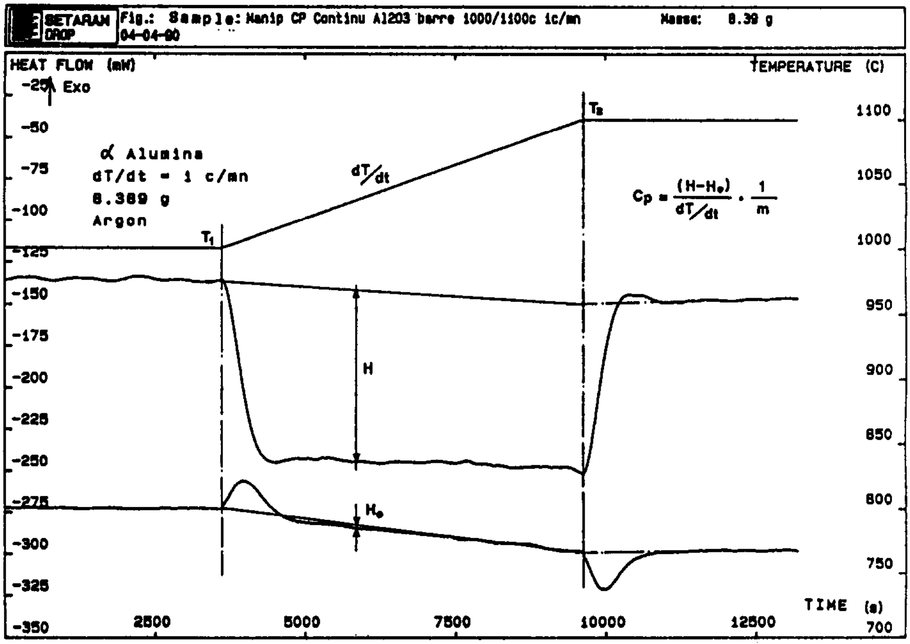

Fig. 3. Continuous heating method for C_p determination.

Continuous heating method

This is probably the most commonly used method on the DSC type instruments. It is easy to use and is not very time consuming. However, in order to deliver good accuracy, some precautions have to be taken [11], especially in the use of a low temperature scanning rate. By reducing the scanning rate, the calorimetric signal is also decreased. As this signal value is used in the determination of the C_p data, it is necessary to increase the sample mass.

With both new detectors, large sample masses are investigated at low scanning rates (1° C min^{-1}). The mass value ranges from 0.5 g with the DSC type detector to 10 g with the drop type detector.

To run the so-called C_p determination at high temperature two successive runs (Fig. 3) have to be performed under the same experimental conditions, using the same crucibles: one with two empty crucibles (blank curve) and one with one crucible containing the sample, the other remaining empty (sample curve).

In the literature, very often drawings of the two traces (sample and blank) are seen with baselines fitting at the beginning and the end of the temperature scanning. Mostly the reality is slightly different, and a shift is noticed between the two baselines. At high temperature, this is more true, and it is necessary to take account of this shift for the determination of the calorimetric signal used for the calculation of C_p.

The determination has already been described [12] and a base line interpolation between the temperatures at the beginning and the end of the scanning is performed as seen in Fig. 3.

For the investigation of α-alumina (sapphire), such a measurement is run between 1000 and 1100 °C at 1 °C min^{-1}, with a sample mass equal to 8.39 g. The C_p value (J g^{-1} °C^{-1}) is obtained from the following ratio

$$C_p = \frac{H - H_0}{V} \cdot \frac{1}{m}$$

in which $H - H_0$ is the signal deviation (W) as described in Fig. 3, $V = dT/dt$ is the temperature scanning rate (°C s^{-1}) and m is the sample mass (g). The reproducibility of the measurement was evaluated on three successive runs with α-alumina (for each run, the container was extracted from the furnace, then reintroduced). It was around 3%.

The C_p determination of α-alumina was used as a calibrating technique for the high temperature calorimeter. According to this calibration, any type of ceramic material can be investigated, by this continuous heating method.

Step heating method

Compared with the continuous heating method, the step heating technique is more time consuming, but its main advantage is that the sample is

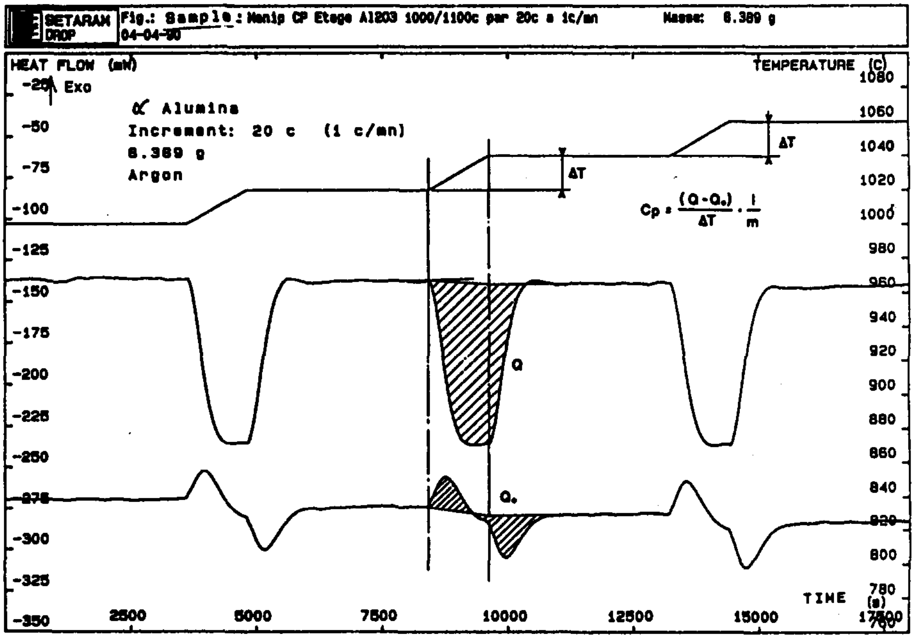

Fig. 4. Step heating method for C_p determination.

in thermal equilibrium after each step of temperature. Instead of measurement by deviation (continuous method), an area integration is used in the step heating method. In this case the measurement is not dependent on the fluctuations of the signal.

Again, either type of detector can be used. In the step heating technique, a step of temperature is scanned from a temperature T_1 to a temperature T_2. Again two successive runs (Fig. 4) with and without sample have to be carried out. Instead of measuring a deviation, the areas under both traces (blank and sample) are integrated. The baseline interpolation is identical [12].

In such a case, the mean C_p values (J g^{-1} °C^{-1}) between T_1 and T_2 is obtained from the ratio

$$\overline{C_p} = \frac{Q - Q_0}{\Delta T} \cdot \frac{1}{m}$$

in which $Q - Q_0$ is the area difference (J) as described in Fig. 4, ΔT is the temperature increment (°C) and m is the sample mass (g).

The C_p of the same α-alumina sample is measured according to this technique (1000–1060°C in steps of 20°C, 8.39 g) (Fig. 4). On three successive runs with α-alumina, the reproducibility of measurement is better than with the previous method, and is around 2%.

α-Alumina is again used as a calibration standard for the C_p determination of ceramics at high temperature.

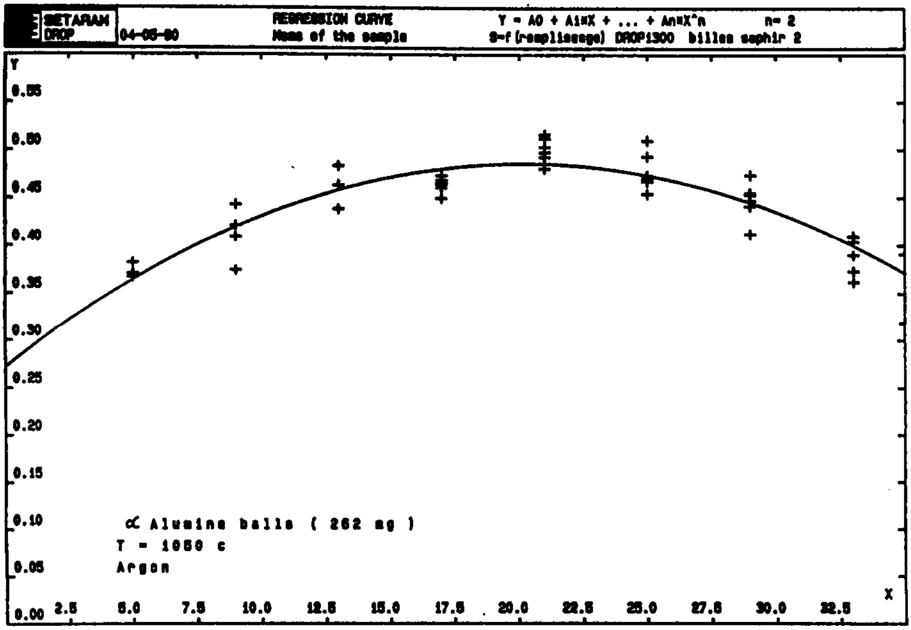

Fig. 5. Drop method for C_p determination.

Drop method

The C_p determination by the drop method is not as well known as the two previous ones. However at high temperature, it is practically the only method to give relatively good accuracy (around 5%), and it is quite an easy technique to use. However, unlike the two previous methods, the drop method does not measure the specific heat of a material directly. The determination of enthalpy at two closed temperatures, T_1 and T_2, is needed to reach the mean C_p value between T_1 and T_2.

For the drop experiment, an introduced sample is hermetically fixed at the top of the furnace. The samples are dropped into the calorimeter under controlled atmosphere. As the experiment is run at constant temperature, a better stability of the baseline is reached compared with the scanning technique. The integration of peaks is made easier (Fig. 5).

For each run, a sample at room temperature is dropped into a region at a temperature T_1, in a container located in the furnace. The corresponding peak is integrated. Several successive drops of identical samples or different samples or different materials can be made in the container at the same temperature. The temperature is then raised to T_2, and the sample drops are

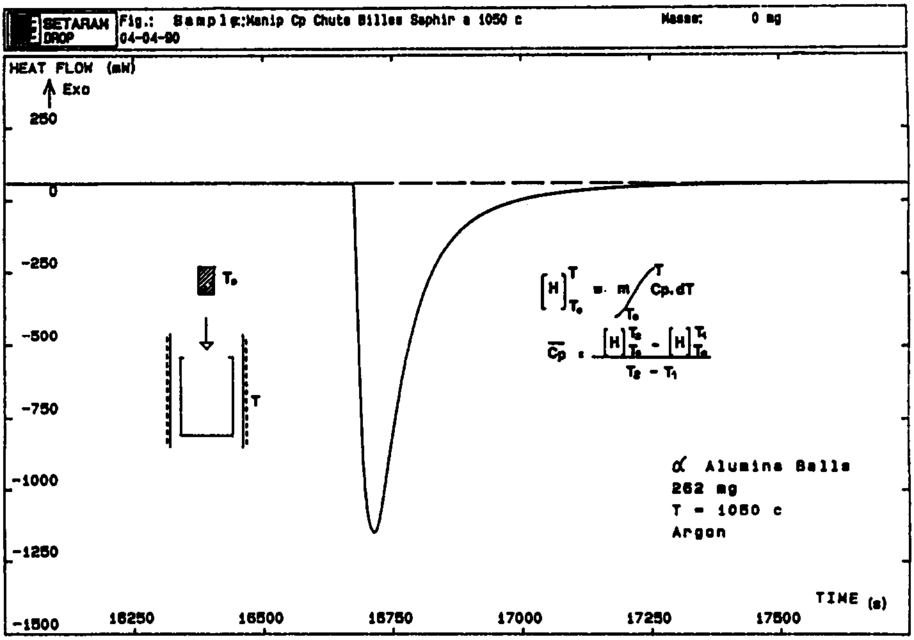

Fig. 6. Influence of sample filling on sensitivity of the drop method for determination of C_p.

repeated. After measuring the different enthalpies at T_1 and T_2, the mean C_p value is obtained

$$[H]_{T_0}^{T_1} = m\int_{T_0}^{T_1} C_p \, \mathrm{d}T$$

$$\overline{C_p} = \frac{[H]_{T_0}^{T_2} - [H]_{T_0}^{T_1}}{T_2 - T_1} \cdot \frac{1}{m}$$

α-Alumina is again used for calibration of the method.

In this technique, one experimental parameter has to be checked: the detector sensitivity versus the sample filling. The transducer used in the new calorimetric detector enables this variation to be limited. To evaluate this variation, 50 balls of α-alumina (mass 262 mg) are dropped into the detector at 1050 °C in order to totally fill the container (Fig. 6). A mean sensitivity equal to 0.44 μV mW^{-1} with a standard deviation of 0.05 μV mW^{-1} was measured.

This technique is also very convenient for measuring the total heat capacity of ceramic materials between two temperatures.

CONCLUSIONS

Comparing the three methods, it appears that the step heating method is to be recommended for the C_p determination of ceramic materials on the new high temperature calorimeter. However the drop method also has several advantages, especially at very high temperatures where the peak integrations are easier at constant temperature.

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