FAST AND ACCURATE HEAT CAPACITY MEASUREMENT AT HIGH TEMPERATURE

C_p DETERMINATION WITH THE LABSYS 3D C_p DETECTOR

Modern industry is requiring more and more materials to be resistant to very high temperatures. Good characterization of these materials is necessary in order to measure their precise properties to know the limits of their use and which applications they can be best applied to. Properties that are needed include, heat capacity data at high temperatures as well as thermal conductivity and thermal diffusivity data.

Material scientists must therefore accurately measure the heat capacity of samples, especially at high temperatures. Many calorimetric devices and methods have been used for these measurements, but the DSC technique remains the most common. The biggest difficulty, besides simply reaching these high temperatures or building measurement systems with materials than can withstand high temperatures, is to overcome the drop in sensitivity of commonly employed thermocouples when approaching their upper limit of use and to deal with perturbations associated with the radiation effects of the samples being measured. Another difficulty with plate-type DSC technique is the limited amount of material that can be tested.

The solution to these problems is to use the Calvet principle. Calvet (3D) sensors have been successfully used in the accurate determination of specific heat. Based on expertise, a 3D detector was designed for the LABSYS evo DSC for C_p determination at high temperatures.

THE LABSYS 3D C_p DETECTOR

The Cp measurement system has benefited from the development of the LABSYS evo, whose furnace has been improved in terms of the maximum temperature rate and temperature homogeneity. This new furnace can scan temperatures at rates up to 100K.min^{-1} along the entire temperature range, i.e. 20-1600°C. The scanning rate can therefore be increased, thus increasing the magnitude of the heat signal.

Moreover, the wider homogeneous temperature zone allows the design of a larger platinum sample holder with capacity up to 380µL and an optional platinum cover (see figure 1), increasing the mass parameter. The 380µL sample holder is positioned on the alumina structure of the rod.

Figure 1: Cross section of the Labsys thermoanalyzer and the C_p 3D DSC detector

The sensitivity coefficient of the Cp measurement system is increased by building a thermopile made of a series of 18 thermocouples, following the Calvet principle. Platinum and platinum-rhodium threads are successively soldered on the whole surface of both alumina holders. Then, heat exchanged by the sample is fully captured and measured.

LABSYS evo
20°C to 1600°C

KEY WORDS
C_p DETERMINATION
3D DSC DETECTOR

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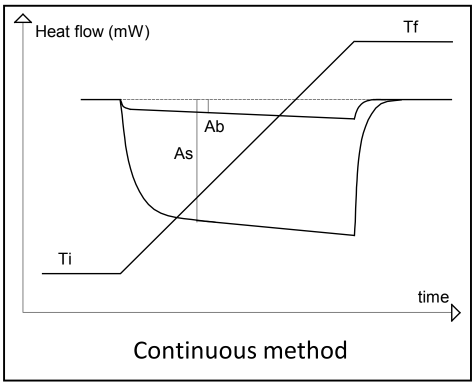
DSC TECHNIQUES FOR MEASURING THE HEAT CAPACITY

The ideal technique for measuring the heat capacity of a material is the calorimetric technique. The DSC signal for a given sample at a temperature T is equal to:

$$\frac{dq}{dt} = mC_p \frac{dT}{dt}$$

where
- dq/dt is the DSC signal
- dT/dt is the temperature scanning rate



The first DSC technique for measuring the heat capacity is called the continuous heating (or cooling) mode (Figure 2). A linear heating rate is applied between T_1 and T_2.

The A_s curve corresponding to the DSC signal of the sample is corrected from the A_b curve corresponding to the DSC signal of the blank experiment (obtained with two empty crucibles).

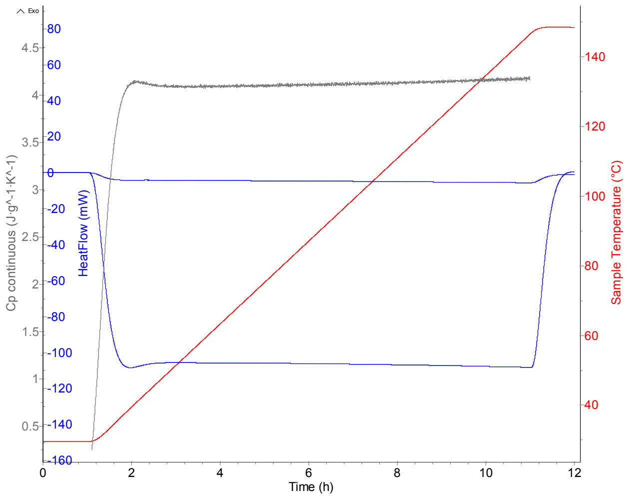


Figure 2: C_p determination using the continuous heating mode

The second DSC technique, called the step heating (or cooling) mode is based on the application of an incremental temperature ramp (Figure 3). In this case the C_p determination is related to the integration of the DSC signal on a given temperature ramp, according to the following relationship:

$$\int_{T_1}^{T_2} \frac{dq}{dt} dt = m \int_{T_1}^{T_2} Cp \frac{dT}{dt} dt \quad \text{which yields:} \quad (Q)_{T_1}^{T_2} = m\overline{Cp}\Delta T$$

The Q_s area corresponding to the sample curve is corrected from the Q_b area which corresponds to the blank curve (with two empty crucibles). In this case a mean C_p value is measured for the given temperature range.

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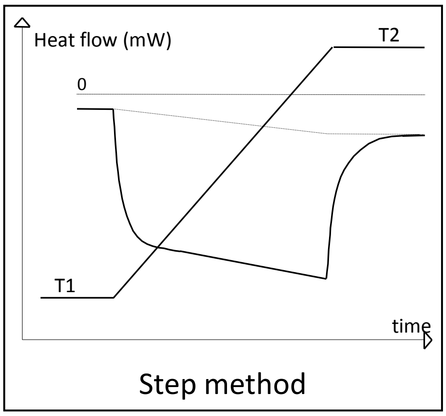

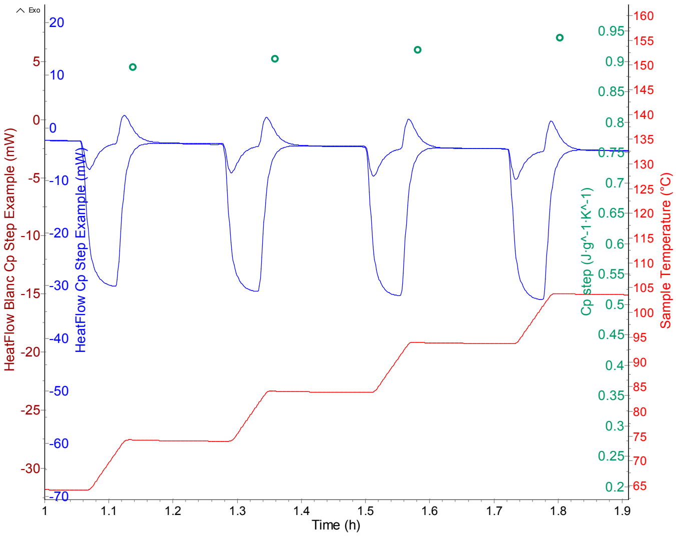

Figure 3: C_p determination in the step heating mode

With the Labsys C_p detector it is possible to measure the C_p of solids from room temperature up to 1600°C. Some examples are given below to illustrate the capacity and the accuracy of the 3D DSC detector.

APPLICATIONS

1 - C_p OF ALUMINA NANOPOWDER CONTINUOUS HEATING)

1 - C_p of alumina nanopowder (continuous heating) 361 mg of alumina nanopowder is used for the C_p determination from room temperature to 1400°C with the continuous method at 20°C.min^{-1} . The sapphire calibration is used for this determination. Two types of confidence intervals are drawn on Figure 4 at ±1% and ±5% of the sapphire C_p value.

Above 300°C, the C_p of alumina nanopowder stays within ±1% of the sapphire C_p interval up to 1400°C.

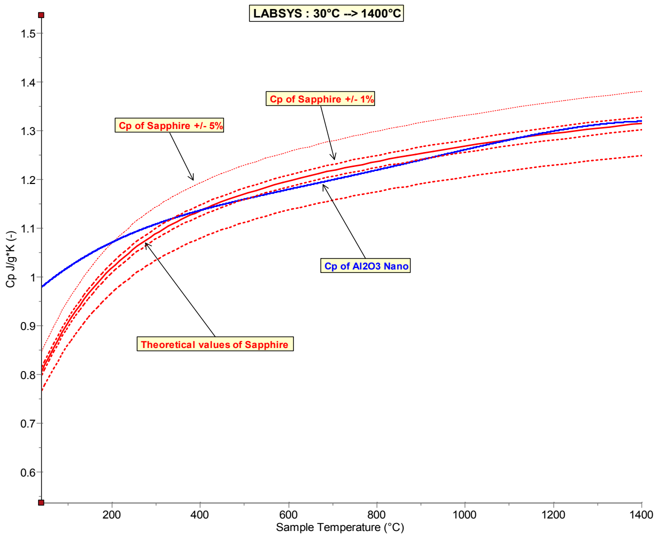

Figure 4: Cp determination of alumina nanopowder using the continuous heating mode

2 - C_p OF TUNGSTEN (STEP HEATING)

4213 mg of tungsten is used for the C_p determination from room temperature to 1500°C using the step heating mode under argon. The selected scanning rate for the ramp is 8°C.min^{-1} and an isothermal step of 1200 seconds is applied after each ramp. A calibration using sapphire was applied for this determination.

The obtained Cp values of tungsten are compared with the JANAF values. A confidence interval of ±5% is drawn on figure 5. It shows that the accuracy of the C_p determination for tungsten using the 3D C_p rod is better than ±5%.

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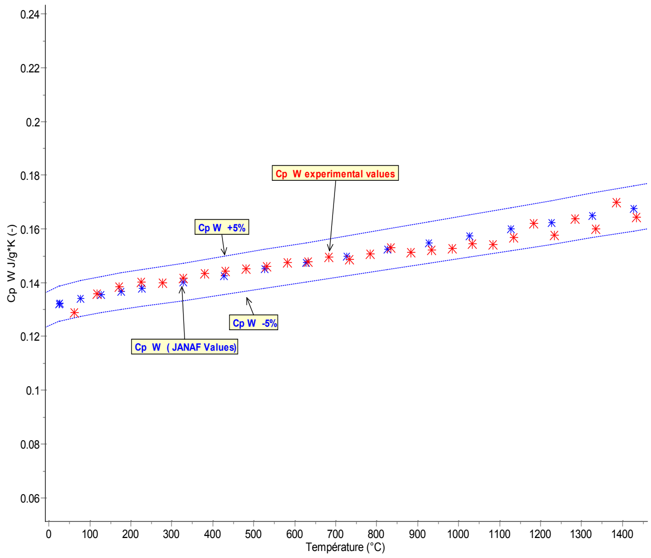
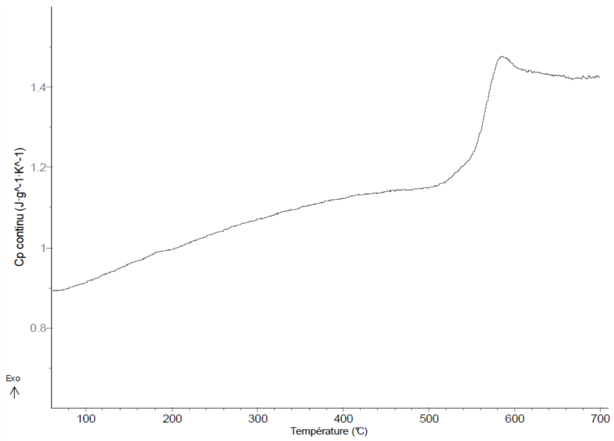


Figure 5: Cp determination of tungsten in the step heating mode

3 - C_p OF GLASS AND GLASS TRANSITION DETERMINATION (CONTINUOUS HEATING)

508 mg of white glass is used for the Cp determination from room temperature to 700°C at 10°C.min^{-1} under argon with the continuous heating mode. Figure 6 shows the C_p variation and clearly shows a jump in the C_p curve after 500°C corresponding to the glass transition of the material. This C_p jump (see table) characterizes the amorphous content of the material.



T(°C)	Cp (J.g^{-1}.K^{-1})
100	0.920
200	1.000
300	1.072
400	1.122
500	1.149
600	1.455
700	1.428

Figure 6: Cp determination of à glass in the continuous mode

CONCLUSION

With the 3D DSC technology, it is possible to accurately measure the heat capacity of materials over a broad range of temperatures up to 1600°C.

The main interest in the technology is the ability to work with a large amount of sample with detectors that completely surround the sample, providing a very good integration of the thermal exchanges.

Tests can be run using both continuous and stepwise methods.

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