Thermochimica Acta, 148 (1989) 499–505
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

A HEAT FLUX DSC FOR ENTHALPY AND SPECIFIC HEAT DETERMINATIONS TO 1700 K

E. Kaisersberger, J. Janoschek, E. Wassmer
NETZSCH-Gerätebau GmbH, Wittelsbacher Str. 42, D-8672 Selb, FRG

ABSTRACT

With a new heat flux DSC sensor, and using a newly designed platinum-rhodium furnace, the temperature range for enthalpy determinations could be extended to 1500°C and precise specific heat capacity measurements are now possible to 1400°C.

INTRODUCTION

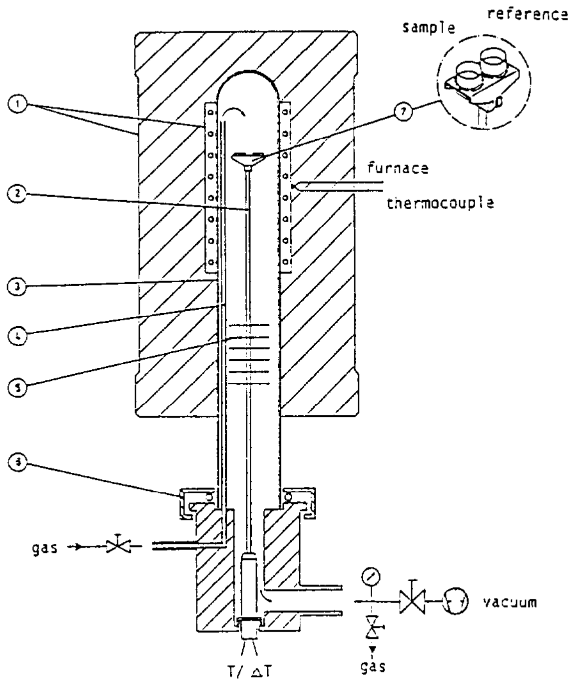
Conventional heat flux DSC systems show good function in the temperature range where heat transfer within the system is mainly based on conduction and convection. Radiation losses are usually responsible for baseline problems and non reproducible results above 600°C. The NETZSCH model DSC 404 has an extended temperature range to 1500°C /1/. A newly developed heat flux DSC sensor as well as a new platinum-rhodium furnace for uniform heat transfer to the sensor are described.

INSTRUMENTATION

The set up of the heat flux DSC model 404 is shown in Fig. 1. The DSC sensor is arranged inside the platinum-rhodium furnace, accessories for evacuation and gas flow are provided. For loading the sample, the furnace is raised by a precise hoisting device. Furnace and sample holder positions are individually adjustable to achieve a reproducible and homogeneous heat transfer to the DSC sensor. An evenly wound Pt-Rh resistance heater is used up to 1500°C and heating rates between 0.1 and 50 °C/min can be selected for the experiments. Different heaters are used for low temperature applications.

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

0040-6031/89/$03.50



1 = furnace

2 = sample carrier

3 = protective tube

4 = gas flow tube

5 = radiation shield

6 = sealing ring (vacuum tight)

7 = measuring head

Fig. 1 DSC 404, scheme of the sample area with connections for purge gas and vacuum pump.

The heat flux DSC sensor is constructed from a thermocouple alloy (platinum-rhodium or nickel-chromium) and is arranged on top of an alumina capillary support. The design and function principle of this DSC sensor is shown in Fig. 2. The top view shows the location for sample (S) and reference (R) crucibles, each of these flat plates being connected by three tabs to the surrounding frame of the sensor. The frame, made of thermocouple grade alloy, acts as an isothermal plane during the experiment. Three additional small tabs hold the crucibles in the same position after loading new material. The side view of the DSC sensor indicates the vertical position of the crucibles, which is to reduce radiation losses at higher temperatures. The flat bottomed crucibles have a large contact area with the plate type thermocouples.

The heat flow scheme in the lower section of Fig. 2 illustrates the principle of heat transfer inside the furnace and along the DSC sensor. During heating by the symmetrically arranged thermal resistors, temperature gradients between the two crucibles build up due to different heat capacities. Physical differences between the crucibles, such as in size or shape, will also result in the presence of thermal gradients especially when heat transfer by radiation predominates. Temperature differences between the two crucibles are then measured by the thermocouples.

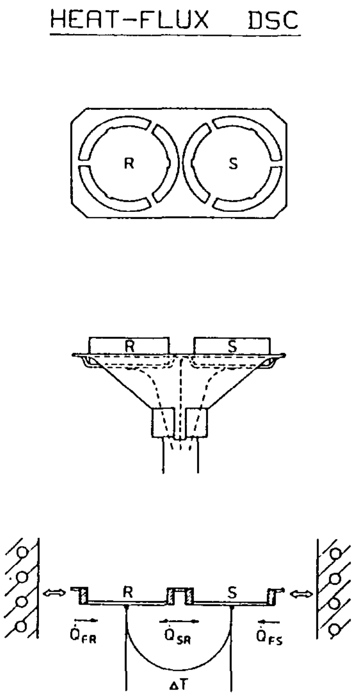
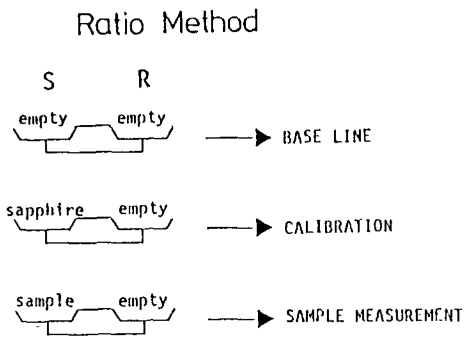


Fig. 2 Heat flux DSC sensor, schematic
(top view, side view and heat flux scheme)

RESULTS AND DISCUSSIONS

Heat capacity determinations by heat flux DSC are best done according to the ratio method (Fig. 3). By three consecutive runs (baseline, calibration, sample test) only the comparison of the deviations of the DSC curves for the standard and the sample to the baseline is necessary. By duplicating experimental conditions, disturbing influences, which would distort results prior to calculations, are eliminated.



$$c_p = \frac{m_{st} \cdot \Delta U_{sa}}{m_{sa} \cdot \Delta U_{st}} \cdot c_{pst} \quad [J/g\,K]$$

ΔU_{sa}	=	potential difference (sample)	(μV)
ΔU_{st}	=	potential difference (standard)	(μV)
m_{sa}	=	weight of sample (sample)	(mg)
m_{st}	=	weight of sample (standard)	(mg)
c_{pst}	=	c_p-literature values (standard)	(J/g.K)

Fig. 3 c_p determination according to the ratio method

In the temperature range 25 to 1400°C specific heat capacity measurements were most successful using platinum-rhodium crucibles with lids at heating rates between 10 and 30 °C/min in a high purity argon atmosphere. Sapphire disks (weight between 25 and 100 mg) are preferred for calibration. Metallic samples are isolated from direct contact with the platinum-crucible by thin alumina sheets and oxidation is prevented using nitrogen atmosphere with a low percentage of hydrogen.

The accuracy of specific heat capacity determinations was tested with some well defined materials such as glass ceramics, Poco graphite, molybdenum, sapphire, UO_2. Fig. 4 shows measured c_p values compared to existing literature data for Pyroceram 9606, a glass ceramic.

The c_p values of Pyroceram 9606, determined according to the ratio method, differ from literature by not more than 1.6% at any temperature, the average deviation being 0.8%. Similar good agreement was found for Poco graphite (AMX 5Q1). The requirement for oxygen free atmosphere is of highest importance for this material (Fig. 5).

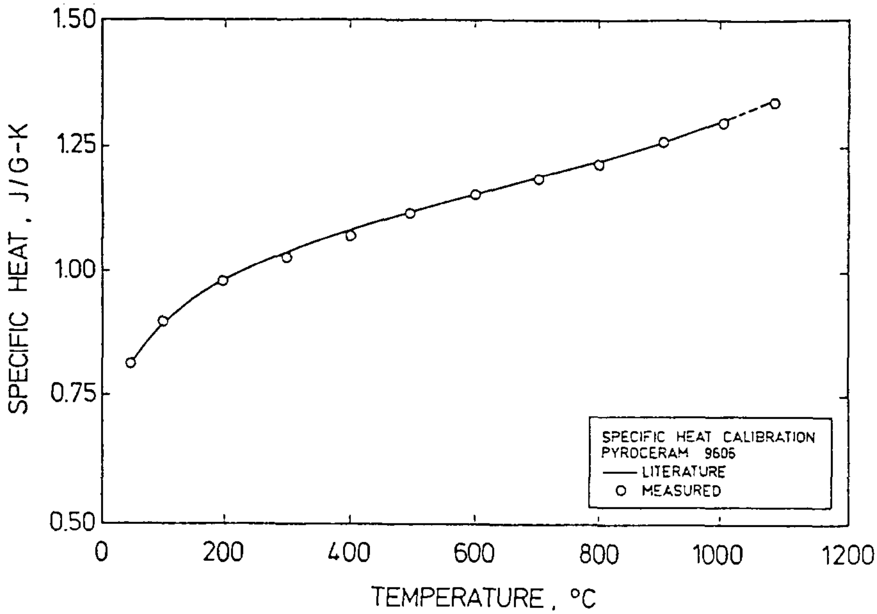


Fig. 4 Specific heat capacity of Pyroceram 9606

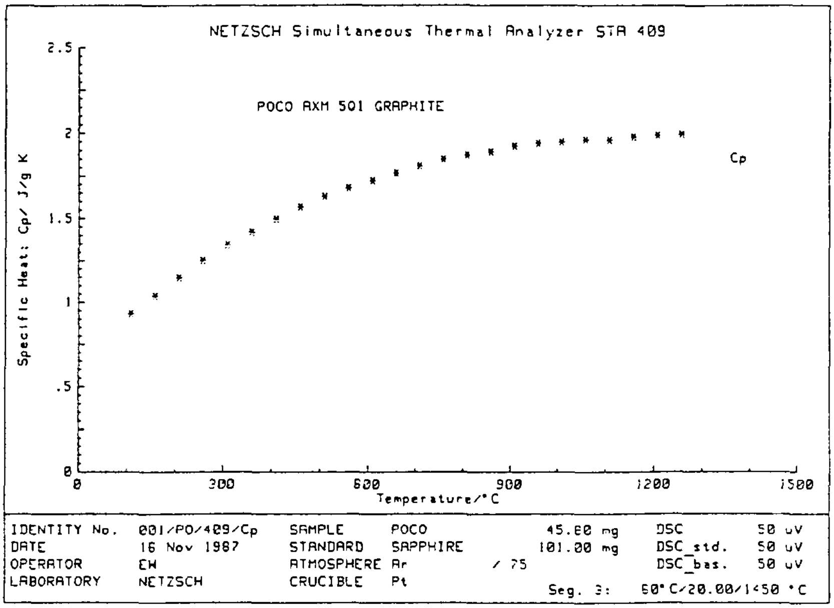
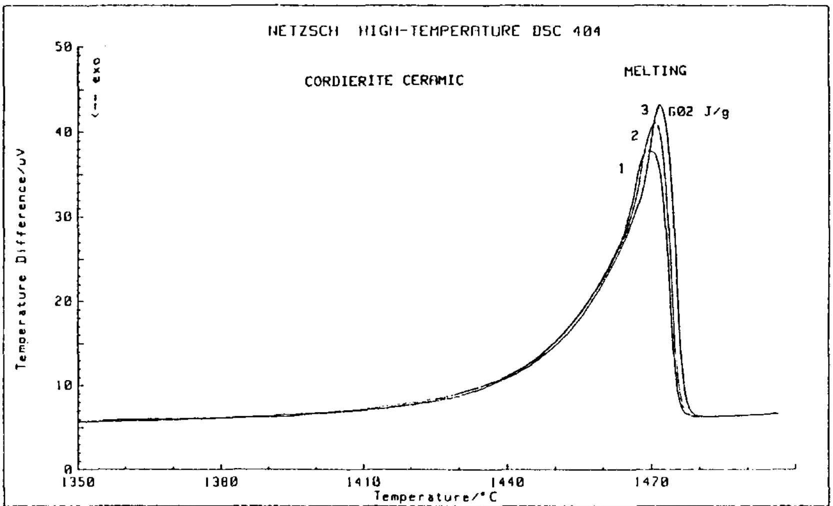


Fig. 5 Specific heat capacity of Poco graphite

Baseline stability, reproducibility and high temperature preformance of this new heat flux DSC are demonstrated with quality control studies on cordierite ceramics (Fig. 6).



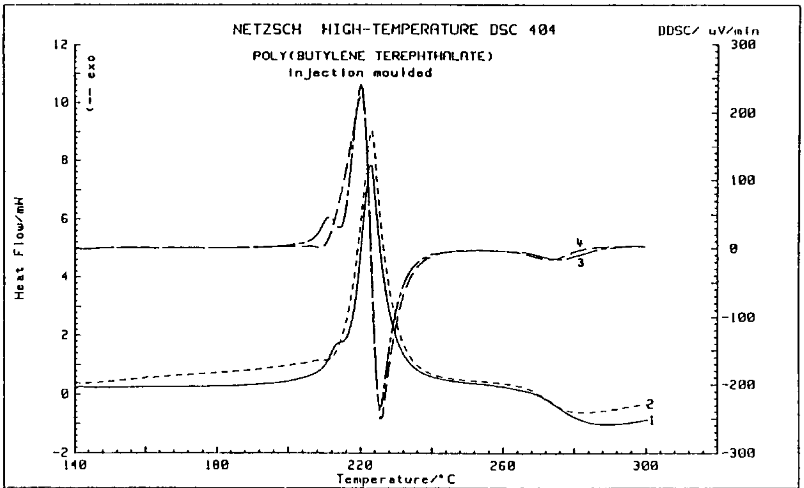
#	SAMPLE	/ mg	DATE	IDENTITY No.	Seg.	RANGE:	Corr.
1	bad quality	20.3	20 Jul 1988	820.891/88	2:	700/20.00/1500	
2	good	20.5	20 Jul 1988	820.891/88	1:	10/20.00/1500	s
3	best quality	20.2	20 Jul 1988	820.891/88	2:	700/20.00/1500	s

Fig. 6 Melting of cordierite ceramic of different thermoshock resistance

The different quality is related to different purity of the samples as indicated by Fig. 6 with lower melting enthalpy for the poorer qualities.

The high sensitivity of the DSC 404 equipped with type E sensor (thermocouple NiCr-CuNi) can be seen from Fig. 7, showing the melting behaviour of injection moulded poly (butylene-terephthalate). Shape and size of the melting peaks at 220°C are quite different for samples taken from different sections of an injection moulded part.

The different melting behaviour indicates clearly the different cooling conditions inside the mould and therefore the changed recrystallization characteristics.



#	SAMPLE	/ mg	DATE	IDENTITY No.		Seg.	RANGE:	Corr.
1	250/70 CENTER	5.2	23 Sep 1987	5		1:	20/20.00/ 350	Bas/
2	250/70 EDGE	5.0	24 Sep 1987	6		1:	20/20.00/ 350	Bas/Sen3s
3	250/70 CENTER	5.2	23 Sep 1987	5	DERIVATION	1:	20/20.00/ 350	
4	250/70 EDGE	5.0	24 Sep 1987	6	"	1:	20/20.00/ 350	

Fig. 7 Melting of poly (butylene-terephthalate), samples taken from edge and center of an injection moulded part.

CONCLUSION

Heat flux DSC can be applied successfully for enthalpy determinations up to 1500°C and specific heat capacity measurements to 1400°C. The special design of the DSC sensor and its adjustable position inside furnaces with very homogeneous temperature distribution provide reproducible baselines with minimum drift over a broad temperature range. The DSC sample holder can also be fitted for simultaneous DSC-TG when arranged on corresponding top-loading thermoanalyzers.

REFERENCES

/1/ E. Wassmer a.o., Thermochimica Acta, 112 (1987) 131-136