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Calorimetric sensitivity and thermal resolution of a novel miniaturized ceramic DSC chip in LTCC technology

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ABSTRACT

The calorimetric properties of a novel miniaturized ceramic differential scanning calorimeter device (MC-DSC) with integrated heater and crucible are presented. All features of a conventional DSC apparatus (including oven) are integrated into this DSC device of the size 11 mm × 39 mm × 1.5 mm. The MC-DSC device is suitable for one-way use, since it is fully manufactured in the low-cost planar low temperature co-fired ceramics technology. First characterization of this device is performed using indium, tin and zinc samples. The calorimetric sensitivity at 156.6 °C is 0.24 J/°C s. It depends linearly on temperature in the range of at least 150 °C and 420 °C. The calorimetric sensitivity is constant up to an enthalpy of fusion of at least $\Delta H = 750$ mJ (at 156.6 °C). The thermal analysis of indium in direct contact to the crucible of the chip even reveals a constant calorimetric sensitivity up to an enthalpy of fusion of at least $\Delta H = 1000$ mJ. The repeatability of the peak area is within ±0.3% (11 mg indium, 10 measurements). The thermal resolution determined using 4,4′-azoxyanisole under TAWN test conditions is 0.12 (i.e. 88%). The thermal resolution determined using Dotriacontane is 0.58 (i.e. 42%). Simulations of a strongly simplified finite element model of the MC-DSC device agree well with measurement results allowing a model-based prediction of its basic characteristics.

1. Introduction

Conventional differential scanning calorimeters (DSC) are highly complex and sophisticated apparatuses to obtain thermodynamic properties of materials. Typical DSC apparatuses are tabletop units to be used in laboratories. On a novel and very inexpensive miniaturized ceramic differential scanning calorimeter (MC-DSC) is reported here. All features of a conventional DSC apparatus (including oven) are integrated into a chip of the size of 11 mm × 39 mm × 1.5 mm. Due to its small size, it consumes little power so that it can even be used with a laptop battery. The entire chip is capable of one-way use, since it is fully manufactured in the low-cost Low Temperature Co-Fired Ceramics technology. Therefore, samples that are very aggressive at elevated temperatures because they disintegrate and emit corrosive gases (thus altering the inner structure of the oven walls and of the calorimetric sensors), can be measured due to the possible single use characteristics of the MC-DSC device.

The new MC-DSC device presented in this paper comprises all functional elements of a conventional DSC (temperature sensors, crucibles and a heater). For that purpose LTCC manufacturing technology was applied. It is suitable for production of threedimensional miniaturized devices containing buried thick film functional elements and geometrical structures ranging from micrometers up to a two-digit millimeter scale. At the same time, LTCC is suitable for a low-cost production of both small lot sizes (rapid prototyping) due to short start-up times and also for mass production due to parallel and batch processing capabilities [1]. An overview on the LTCC technology is given in [2,3]; some detailed processes of the here-applied LTCC technology are described in [4,5].

A short description of the design and of the manufacturing of the MC-DSC device will be given prior to the presentation of the measurement results. The focus will be laid on the calorimetric calibration of the chip and on the demonstration of its thermal resolution, which reflects the ability of a DSC instrument to detect and evaluate close thermal events. The reliability of the results is confirmed by a series of repeatability tests.

2. Design comparison and general properties of the MC-DSC device

The measurement principle applied in the MC-DSC device is identical to that of a heat flux DSC. A sketch of a heat flux DSC

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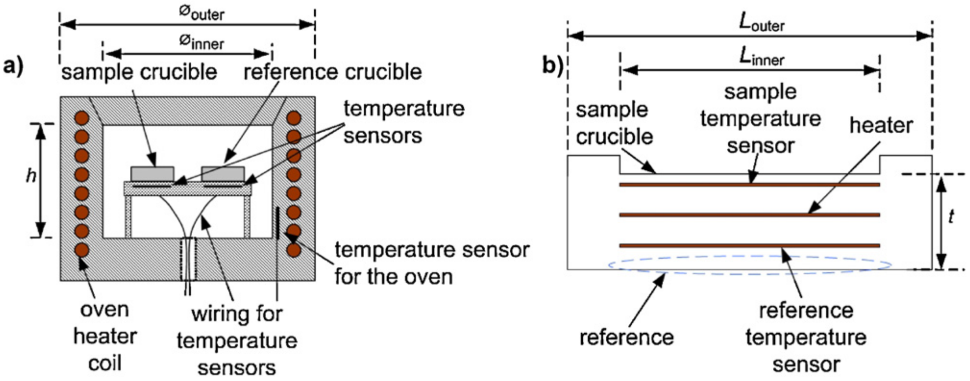

Fig. 1. Design comparison: (a) conventional heat flux DSC. Typical approximate dimensions are: $\phi_{\text{outer}} = 30–35$ mm (outer diameter of the furnace), $\phi_{\text{inner}} = 20–25$ mm (the diameter of the compartment) and $h = 20–30$ mm (the height of the compartment); (b) cross section of the probe head of an MC-DSC. Please note: The small device on the right replaces the DSC apparatus on the left. Dimensions: $L_{\text{outer}} = 11$ mm, $L_{\text{inner}} = 6.5$ mm, $t = 1.2$ mm.

is depicted in Fig. 1a. In this widespread commercial type of DSC two crucibles containing an inert reference and the sample are placed on a thermally conductive support, the so-called DSC sensor. The DSC sensor incorporates two temperature sensors below the crucibles that measure both the sample and the reference temperatures. The whole arrangement is surrounded by an oven that is thermally controlled using a further temperature sensor. During a calibration run, the calibration function of the DSC sensor is determined. This function, which also can be called the calorimetric sensitivity, incorporates all heat transport mechanisms occurring between the sample, the reference position and the DSC sensor. Therefore, it usually depends non-linearly on temperature. During a thermal analysis, the temperature difference between the sample and the reference temperature sensor is measured whilst the oven is heated or cooled at a certain constant heating or cooling rate, respectively. Using the calibration function, the heat flow from the sample to the reference is calculated and is plotted against the sample temperature. The thermodynamic properties of the samples are determined by the evaluation of the measured heat flow. Basic evaluation techniques of a DSC signal are described in [6–8].

The unique feature of the new miniaturized ceramic DSC is the vertical arrangement of the DSC functional elements. The design of this structure can be described by a heat flux DSC which is turned inside out: the oven is represented by a planar heater which is surrounded by a planar sample temperature sensor on the top side and a planar reference temperature sensor on the bottom side of the probe head (see Fig. 1b). A cavity on the top of the probe head serves either directly as a crucible for the samples or as a holder for commercially available DSC crucibles. The reference is an integral part of the probe head below the reference temperature sensor. This simple design allows a very compact DSC sensor that can be manufactured in a single integrated fabrication process using the LTCC technology. The calibration and evaluation of the measurement data is done the same way as in the conventional heat flux DSC.

To avoid an iterative trial-and-error development process and therefore to save time and material costs, a strongly simplified finite element model of the MC-DSC device was set up. It has been used to investigate the response of the chip upon a melting process taking place in the crucible [10]. Using the FEM analysis, we were able to prove the realizability of the new DSC design and also to determine optimal geometrical parameters of the final structure which is shown in Fig. 2.

The probe head is mechanically and electrically connected to the contact pads via two beams. A cooling fin has been implemented to protect the contact pad area and also the plastic connector from overheating. The mass of the probe head of approx. 400 mg allows a very low power consumption due to the low heat capacity. Details on the manufacturing process and on the FEM modeling of the MC-DSC have been published in [10]. The focus of this work is on the calorimetric calibration of the device and on its thermal resolution.

One important design specification of the MC-DSC device was to keep the compatibility to the conventional handling of the samples. To meet this requirement, the crucible of the chip has a diameter of 6.5 mm, which is enough to accommodate aluminum crucibles used in most conventional DSC apparatuses. Thus, the sample material preparation procedures are fully compatible with those already used in the DSC/DTA analytics. This allows a fast familiarization of the user with the new device, since no additional techniques or tools are needed to accomplish a DSC measurement.

The maximum working temperature of this initial MC-DSC device is approx. 500 °C, covering the most common temperature range in the field of thermal analysis. Considering the low power consumption of only 12 W at 500 °C, mobile thermal analyses using the MC-DSC device are also conceivable: a battery of a mobile computer would be sufficient to carry out several thermal analyses.

The replacement of a contaminated or defective MC-DSC device can be accomplished within minutes by the user itself. Considering also the low costs for manufacturing, the MC-DSC device is even suitable for one-way use at reasonable costs.

3. Measurement results

Ideally, differential scanning calorimeters should show a good linearity of the measurement signal depending on the heat flow rate. It simplifies the signal processing and is also a prerequisite for desmearing of the heat flow rate by deconvolution [6,26]. Unfortunately, due to the spacious extent of a conventional DSC oven (see Fig. 1a) with a long heat flow path in the centimeter range between both temperature sensors as well as between the sensors and the oven wall, several heat transport mechanisms (conduction, radiation and convection) take place on the signal path at the same time. This leads to a non-linear behavior of the measurement signal depending on the heat generated or taken up by the sample [15,25]. Therefore, the heat flow rate between the temperature sensors depends on the sample mass, on the heating rate, and also on temperature. Usually, to meet the specifications on linearity, the signal is corrected/linearized by the evaluation software [7]. However, for this purpose the analyst/operator has to perform on a regular basis several calibration runs to take into account each aspect of dependencies at each heating rate. In contrast, the inner structure of the MC-DSC device is predestined for a highly linear raw measurement