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Miniaturized ceramic differential scanning calorimeter with integrated oven and crucible in LTCC technology

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A B S T R A C T

A miniaturized ceramic differential scanning calorimeter (MC-DSC) with integrated oven and crucible is presented. Despite its small size of only 11 mm × 39 mm × 1.5 mm, all functions of a conventional DSC apparatus are integrated in this novel device – including the oven. The MC-DSC is fully manufactured in thick-film and green glass ceramic tape-based low temperature co-fired ceramics (LTCC) technology. Therefore, production costs are considered to be low. Initial results using indium as a sample material show a good dynamic performance of the MC-DSC. Full width at half maximum of the melting peak is 2.4 °C (sample mass approx. 11 mg, heating rate approx. 50 °C/min). Repeatability of the indium melting point is within ±0.02 °C. The melting peak area increases linearly with the sample mass up to at least 26 mg. Simulations of a strongly simplified finite element model of the MC-DSC are in a good agreement with measurement results allowing a model-based prediction of its basic characteristics.

1. Introduction

Differential scanning calorimetry (DSC) is a wide-spread method to determine phase changes of materials like melting points, boiling points, or glass transition points and to measure the corresponding enthalpies. Additionally, this method can be applied to obtain data of the specific heat. Design, functional principle of DSC devices, as well as basic evaluation techniques of the measured raw data are well-known and are comprehensively described in the literature, i.e. in [1].

Commercially available DSC apparatuses are expensive and complex. They are hardly suitable for thermal analysis of materials which might release aggressive gas phases at elevated temperatures. Such materials would contaminate or even destroy the DSC oven and/or its temperature sensors by altering their characteristics. Costly repair would be the consequence. In such cases, the presented novel "miniaturized ceramic differential scanning calorimeter" (MC-DSC) might be an appropriate solution. This structure comprises all elements of a DSC apparatus – including the oven – in one ceramic monolithic device. In the following sections, the design of MC-DSCs, their functional principles, and initial calculations and results are presented.

2. Design and manufacturing of the miniaturized ceramic DSC

The operation principle of MC-DSCs is based upon that of a heat-flux DSC. In Fig. 1, the principle setup of a heat-flux DSC is shown. It is compared to a simplified model of the probe head of the MC-DSC (Fig. 2).

In the heat-flux DSC, the sample and the reference crucibles are placed on a sample holder with integrated temperature sensors for temperature measurement of the crucibles. This arrangement is located in a temperature-controlled oven. Contrary to this classic design, the distinctive attribute of the MC-DSC is the vertical configuration of planar temperature sensors (sample sensor and reference sensors) above and below a planar heater (Fig. 2). This arrangement allows a very compact, lightweight and low heat capacitance structure with the full functionality of a DSC oven. It is represented by a disk with a cavity on its top side with a diameter of 6.5 mm. It allows either to employ the most commercially available types of aluminum crucibles or it can serve as a crucible itself (see Section 4.2). Another feature of this structure is the integrated reference below the reference temperature sensor, which

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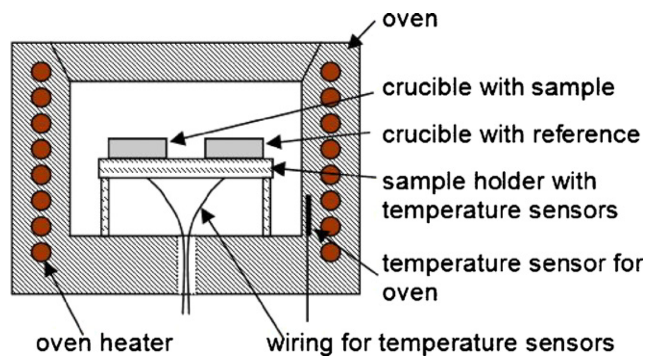

Fig. 1. Heat-flux differential scanning calorimeter according to [1].

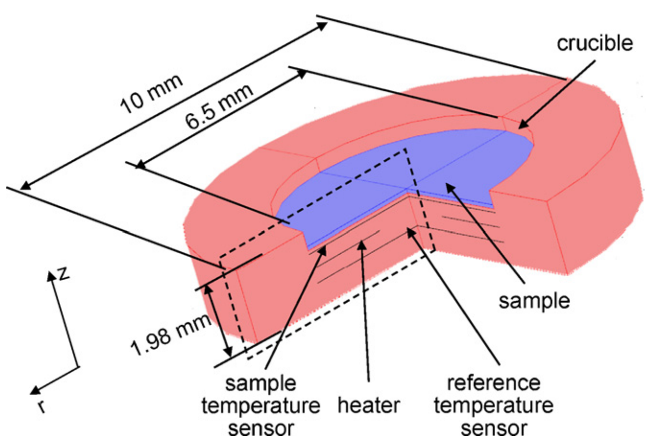

Fig. 2. Sketch of the probe head of the MC-DSC chip (the marked dimensions were used for the simulations, see Section 3). The reference is a part of it enclosed by the reference temperature sensor and the lower edge of the probe head. The chip consists of LTCC material (red) and an indium sample (blue). The axial symmetry of this structure allows a 2D axial symmetry model. The dashed lines form the simulated two-dimensional cross-sectional area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

consists of the same material as the chip body. A 3D-drawing of the entire MC-DSC chip is illustrated in Fig. 3a. A heat sink provides cooling of the connector plug to protect the plastic chip holder (a commercially available edge-card connector) from overheating. The dimensions of the structure are only 11 mm × 39 mm × 1.5 mm. The planar temperature sensors and the heater are made of screen-printed platinum thick-films. The conductors and the contact pads consist of gold thick-films. The chip body is made of several layers of zero-shrinkage LTCC tape (HeraLock® HL 800, Heraeus, Hanau, Germany), which were structured by a frequency-tripled Nd:YAG laser as described in [2,3]. The laminated tapes were sintered at a peak temperature of 880 °C. Further detailed information on the applied LTCC technology can be found in [4] and [5]. A photograph of a realized MC-DSC is shown in Fig. 3b. The weight of the MC-DSC is 1.3 g, while the weight of the probe head is only 400 mg.

3. Model-based estimation of device characteristics

In order to study whether this approach of a planar type heat flux differential scanning calorimeter is feasible and whether it can be realized in LTCC technology, a simple model of such a structure was established to roughly estimate its basic parameters and the resulting characteristics. With the help of this model, the MC-DSC was designed before it has been manufactured. Indium – a standard material for the calibration of DSC apparatuses [6] – served as the sample to characterize the performance of the modeled structure.

The geometry in Fig. 2 representing the MC-DSC has been setup in a two-dimensional axial symmetry to save computation time. Transient simulations were carried out using the heat transfer module of COMSOL® finite element analysis software. Since this initial model served only for a rough estimation of the expected characteristics of the MC-DSC, we considered only two heat transfer mechanisms:

- thermal conduction within the body of the structure and within the sample (here indium) and
- radiation at its outer boundaries.

We kept the model as simple as possible and omitted the convective heat transfer mechanisms to avoid unnecessary complexity of the model and again, to save computation time. This simplification is justified for two reasons:

1. The convective losses at the vertical edges of the structure lead to a radial heat flow influencing the temperature distribution within the crucible. At the same time, the heat flow path from the temperature sensors to the edge is longer than the heat flow path from the sample to the reference temperature sensor by a factor of four, making heat conduction between the sensors a dominant heat transfer component in this case.
2. Furthermore, neglecting the vertical wall of the integrated crucible, the probe head can be considered as a heated horizontal plate with equal surfaces on its top and on its bottom side. Thus, according to Remsburg [16] the free convection on the top and the bottom side of such plate will be different but this difference will also be temperature independent as long as the convective flow stays laminar on both the top and the bottom side of the plate. For a structure of this size the laminar convective flow

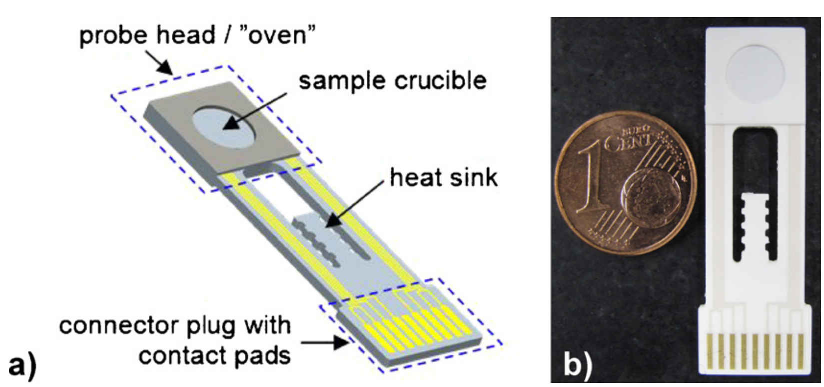

Fig. 3. (a) 3D drawing of the entire MC-DSC chip; (b) photograph of the chip with a 1 €ct coin for size comparison. Thickness and width of the probe head is 1.5 mm and 11 mm, respectively. The length of the entire chip is 39 mm.