Journal of
Ceramic Science
and Technology

J. Ceram. Sci. Tech., 04 [03] 137-144 (2013)
DOI: 10.4416/JCST2013-00008
available online at: http://www.ceramic-science.com

Development of a Miniaturized Ceramic Differential Calorimeter Device in LTCC Technology

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received March 18, 2013; received in revised form April 30, 2013; accepted May 29, 2013

Abstract

Differential Scanning Calorimetry (DSC) is used to identify phase transition temperatures of different materials. Classical DSC devices are designed as stationary equipment and, owing to their weight and construction, mobile use is impossible. Relatively high costs may limit the span of application. To reduce costs and enable mobile applications, our idea was to construct a miniaturized ceramic differential scanning calorimeter in which furnace, temperature sensors, crucible, and reference are fully integrated into one single ceramic device measuring only a few centimetres in size.

In this article, two types of miniaturized ceramic calorimeters are presented. Whereas the first one is based on the power compensation method, the second utilizes the dynamic heat flux method. Both structures were made in Low Temperature Co-Fired Ceramics (LTCC) Technology. Application of ceramics as body material ensures sufficient stability and a wide working temperature range. First tests proved that melting processes with promising dynamic performance can be detected. This article focuses on the development steps that lead to novel well-functioning LTCC-based DSC devices and demonstrate their functionality. It is also intended to show some deadlocks during the development and demonstrate how important FEM modeling is for obtaining well-functioning devices.

Keywords: DSC, LTCC, differential scanning calorimetry

I. Introduction

Differential Scanning Calorimetry (DSC) is a widespread method to determine phase transition enthalpies of materials. DSC analysis is used to analyze and study polymers such as thermoplastics, thermosets, elastomers, or adhesives, as well as foodstuffs, pharmaceuticals, chemicals, and composite materials [1,2]. Owing to their complexity, typical DSC devices are expensive. Conventional DSC equipment is designed for stationary laboratory use and is usually not intended for mobile applications or for fast and *in-situ* analysis. To avoid furnace contamination, some materials are even restricted in conventional DSC devices. Therefore, our idea was to construct a novel DSC chip, in which furnace, temperature sensors, as well as sample crucible and reference are fully integrated into one small ceramic structure. Thus, overall costs and power consumption could be drastically reduced.

The most suitable technology for such a device appears to be Low Temperature Co-fired Ceramics (LTCC). Besides applications in automotive control units for rugged conditions or small high-frequency devices, applications utilizing LTCC in sensor technology, in biochemistry, or in microfluidics are emerging [3–12]. For high-temperature applications, for instance for gas sensors, very interesting solutions have been presented as well [13,14]. The advantages of LTCC are obvious. Easy patterning of unfired tapes enables the design of ceramic substrates with three-dimensional elements. It allows a reduction in power consumption and structural dimensions, especially when hot plates are used [15,16]. Owing to the multilayer setup, integration of heater and temperature sensors inside the monolithic ceramic is possible. More details about the LTCC technology can be found in the overview literature, e.g. in references [17–19].

The operating principles of today's DSCs are based either on the power compensation method (power compensation dynamic scanning calorimeter, PCDSC) or on the dynamic heat flux DSC (HFDSC) [20,21]. Initially, in our study, both methods were taken into account. The important criteria in selection of the working principle included the simplicity of the construction, possible small dimensions, low power consumption and appropriate accuracy. The aim of this article is to show the development steps that lead to a novel well-functioning LTCC-based DSC device and to demonstrate its functionality. It is also intended to show some deadlocks during the development, in order to pass on our experience to other researchers.

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II. Power Compensated DSC-Chip

(1) Design considerations

In power-compensated DSCs (PCDSCs), sample and reference are located in two thermally isolated crucibles. The temperature of each crucible is measured. The two crucibles are typically placed in two separate but identical furnaces and heated at the same heating rate, which is usually kept constant. During the experiments, sample and reference are forced to remain at the same temperature. The power required to keep the temperatures identical in the two furnaces is used as the measurand [20].

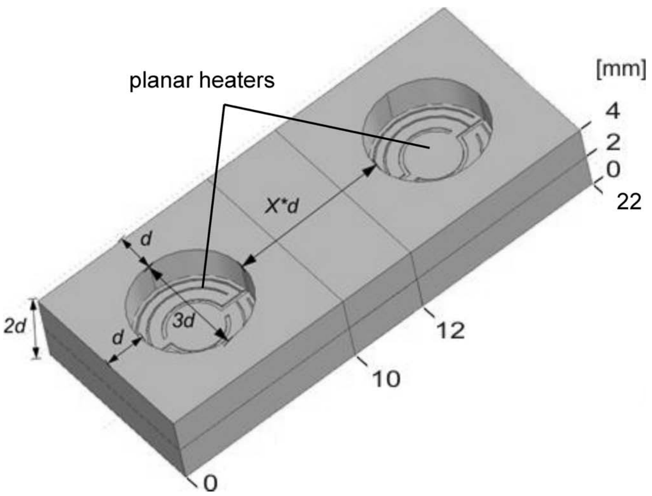

Fig. 1: Sketch of the PCDSC chip. This setup was used for modeling. Only the part with the two crucibles is shown.

To transform the working principle of a PCDSC to a miniaturized chip manufactured in LTCC technology, two important aspects have to be considered: a homogenous temperature distribution in the crucible areas and thermal isolation between crucibles and the ambience. Therefore, an initial simplified 3D-model was designed. In Fig. 1, only the part in which the crucibles are located is shown. This basic setup was steadily improved and a first PCDSC chip was made with an optimized design. In the model, two crucibles with integrated heaters were considered.

To simplify the design process, a parameter d (with d = 2 mm) was introduced (Fig. 1). This parameter defines a minimal ratio between dimensions of the structure, such as thickness, distance between edge of the crucible and edge of the structure, crucible diameter or space between crucibles. A simulation of the temperature distribution was conducted using COMSOL Multiphysics software. At this stage, material parameters were taken from literature or from the material library of COMSOL Multiphysics. The first results showed that the designed space between crucibles is not enough (Fig. 2a). The temperature maximum in both cases is displaced somewhere to the middle of the structure. This is obvious from the horizontal temperature profiles (Fig. 2b), in which each line represents the temperature distribution along the structure starting from the center of the heater (0 mm) to the edge of the model. Besides the displaced temperature maximum, the temperature constancy is poor.

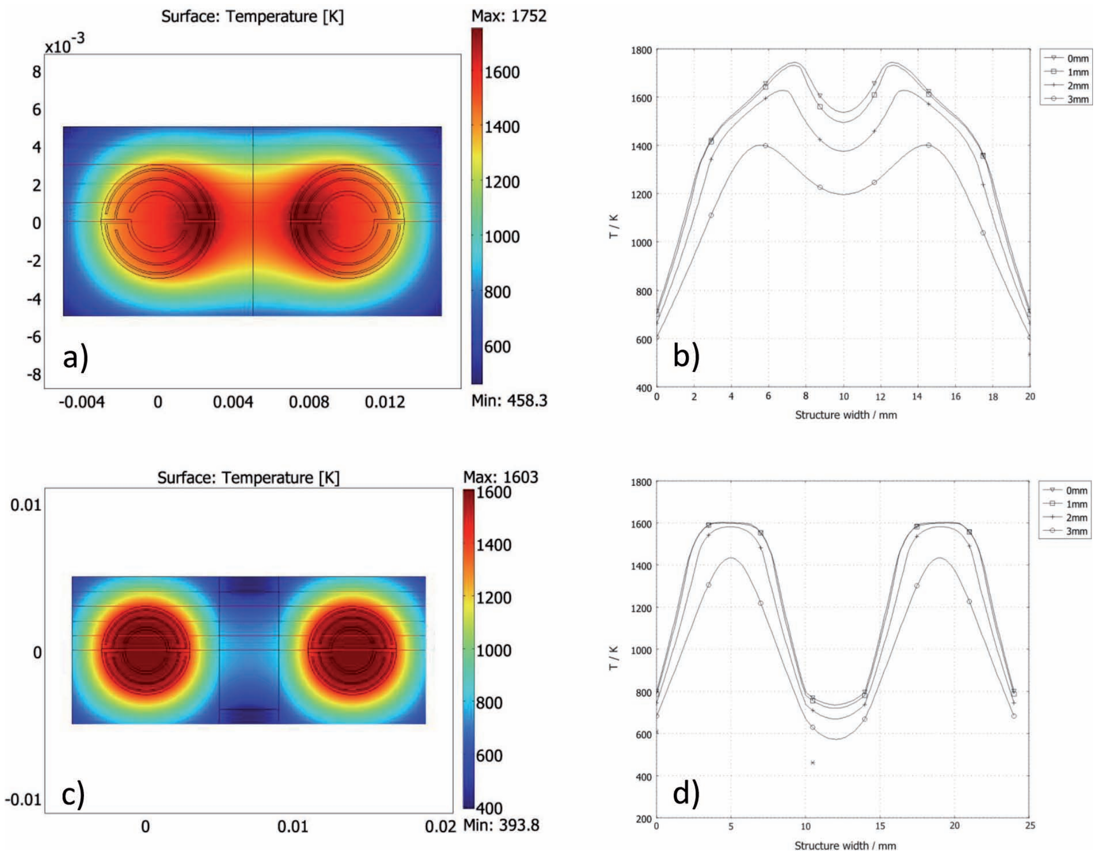

Fig. 2: Modeled temperature distribution and horizontal temperature profiles for the initial structure (a), (b), respectively, and for the structure after removing the ceramic between the crucibles (c), (d).

Therefore, in a first improvement, we increased the distance between the crucibles up to 4*d* (results not shown). This allowed better separation of the heat sources, but owing to heat conduction, the maximum temperature displacement remained in the LTCC ceramics. On the outer sides, heat dissipation within the ceramic material occurred over the length *d*. Moreover, both outer walls as well as the top and bottom walls of the structure are cooled by means of convection. This caused the displacement towards the center of the structure. Therefore, the monolithic ceramic between both crucibles was opened (length 4*d* and width 1*d*). The distance between heater, edges of the structure, and opening was also 1*d*, i.e. the distance from heater to edge is identical on all sides. The opening yielded a decreased maximum temperature but improved the separation of the heat sources (Fig. 2d). The temperature homogeneity in the crucible area was also improved considerably (Fig. 2c).

In the final design, which was later realized (see below), conductors and contact pads were introduced (Fig. 3a). The device consisted of a ceramic body, one layer with the required conductors, contacts, and two heaters that are used for temperature measurement as well. A 50-µm-thin insulating layer covered the planar heaters – only 50 µm thin to ensure that they are placed as close as possible to the specimens. Another part of the structure formed two crucibles for sample and reference. The thermal insulation between both furnaces was realized in form of the above-mentioned opening between the crucibles.

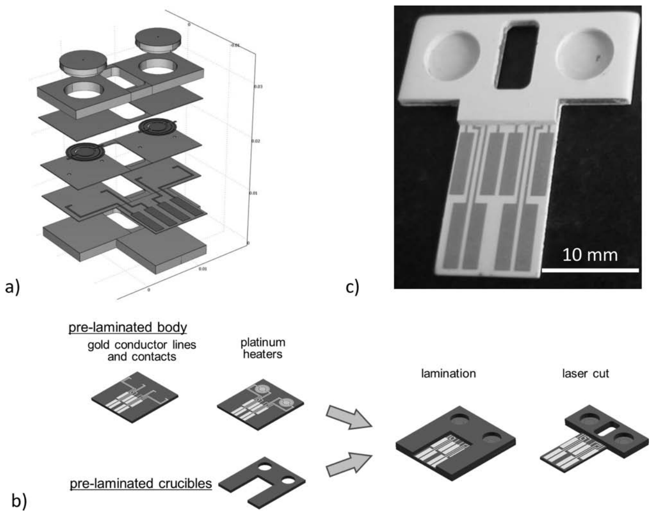

Fig. 3: Final design of the power compensated DSC device (a); Manufacturing of the power compensated DSC chip (b) and photograph of the final device manufactured in LTCC technology (c).

(2) Implementation of simulation results in LTCC technology

Based on the above-presented simulation results, a ceramic version of the power-compensated DSC device was realized. At the bottom of the structure, four additional contacts were introduced for a four-wire measurement of the resistance of the heaters. Since the simulation showed a temperature below 70 °C in the contact area, this modification should not have any significant influence on temperature distribution within the crucibles.

The most important technological steps to implement the power-compensated DSC chips are shown in Fig. 3b. On the pre-laminated body of six zero-shrinkage tapes (HL800, Heraeus, each 135 µm thick), gold lines, gold contacts (TC7102, Heraeus), and two platinum heaters (LPA88 – 11S, Heraeus) were screen-printed. Another part of the structure was built of twelve layers. Out of them, crucibles for sample and reference were laser-structured. The laminate with screen-printed platinum heaters was covered by a tape with a thickness of 50 µm. This very thin tape ensured that heaters, which are also used for temperature measurement, are placed as close as possible to the specimens. Both laminates with the thin tape in between them were laminated together. The last step before sintering was to cut out openings between the crucibles. The structures were sintered at 865 °C using typical LTCC firing profile for HL800 tape. Fig. 3c is a photograph of the miniaturized power-compensated DSC device in LTCC technology. With dimensions of 28 × 25 mm^2, the weight of the whole device was about 1080 mg (one crucible 400 mg). The thickness of the structure head with the crucibles was about 3.6 mm, whereas in the contact area, the thickness was only 1.2 mm.

(3) Characterization of the PCDSC-chip

At first, the buried platinum heaters were characterized. In previous works, it had been shown that platinum ink LP88 – 11S can be applied as a material for buried heaters and temperature sensors [16]. Moreover, the platinum layer can be co-fired with LTCC tapes with a temperature coefficient of resistance, TCR, being similar to Pt100 temperature sensors. The measured temperature dependence was fitted according to DIN IEC 751 [22] (temperature range 0 °C – 850 °C):

$$R = R_0 \cdot (1 + \alpha \cdot T + \beta \cdot T^2) \qquad (1)$$

The Hot Temperature Coefficient of Resistance (HTCR) was calculated according to:

$$HTCR = \frac{1}{R(25°C)} \cdot \frac{R(125°C) - R(25°C)}{125°C - 25°C} \qquad (2)$$

The values of a and β were determined in a series of four test runs to $a = 3.94 \times 10^{-3}$/K and $\beta = -6.12 \times 10^{-7}/K^2$ with an *HTCR* of 3530 ppm/K. The α-values scattered by ± 0.03 × 10^{-3}/K (min. and max.). For comparison: the reference value for Pt100 sensors acc. to [22] is $a = 3.908 \times 10^{-3}$/K. In other words, the temperature-dependent resistance behavior is similar to that of pure platinum temperature sensors.

The SEM investigations showed very good compatibility of the platinum ink with the non-shrinkage tape HL800. As an example, a cross-section of a buried heater is shown in Fig. 4. The platinum layer thickness is about 4 µm. For structures buried into LTCC ceramics, the thickness of the thick-film layer is typically a little smaller then when applied on top of an already-fired substrate [23]. No delamination was detected. On alumina substrates, the paste LP88 – 11 is rather porous, whereas in case of an application on top of or inside LTCC dense homogenous layers can be achieved.

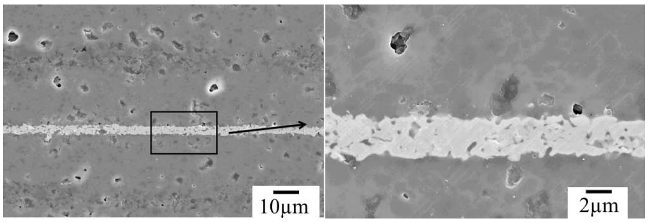

Fig. 4: Cross-section of buried platinum heater.

The results of the above-presented modeled temperature distributions were verified with an infrared camera (Varioscan 3011ST). Fig. 5 shows the heat distribution image of the chip.

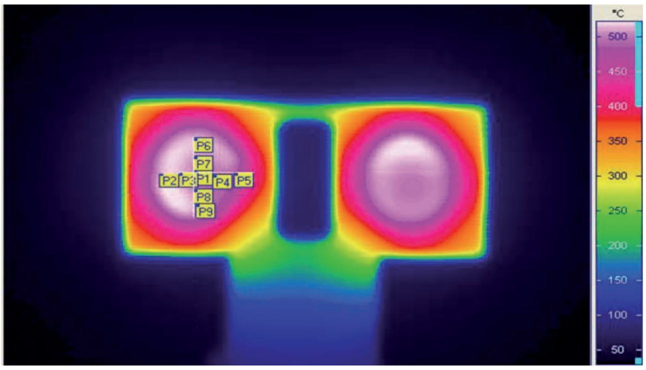

Fig. 5: Measured temperature distribution of the power compensated DSC chip. Temperatures P1: 499.9 °C, P2: 508.2 °C, P3: 510.7 °C, P4: 494.4 °C, P5: 485.0 °C, P6: 510.0 °C, P7: 507.4 °C, P8: 501.2 °C, P9: 473.8 °C.

The vertical and horizontal profiles show good homogeneity in the crucible areas. At the maximum temperature of 500 °C, the temperature difference amounts to about 10 °C (points P1, P3, P4, P7, P8). Compared to Fig. 2c, the point of maximum temperature is shifted from the center of the crucible to its top-left corner. The reason for that is the heat conduction within the substrate towards the chip contacts. The contacts themselves are cold compared to the probe head. These data show that a small modification of the heater design can further improve the chip.

The temperature-dependent characteristics of the resistors of both structures are compared. The resistors were characterized in a tube furnace in the temperature range up to 800 °C. The measurements were conducted in four-wire configuration. Between room temperature and 500 °C, their resistances depend almost linearly on temperature, i.e. for up to 500 °C, a linear regression instead of polynomial one can be applied. This will simplify the temperature control of the device. Moreover, relative deviation of the resistance between both heaters is very small, and amounts to only about 1 % in the entire temperature range.

The very first calorimetric measurements were made with polyamide PA 66. First, the material was measured in a commercial DSC device (Mettler-Toledo 821e). It showed a melting point at 263 °C, with a peak width of $\Delta T \approx 16$ K.

In our test, 9.97 mg of polyamide were placed in the crucible of the power-compensated LTCC-DSC device. The other crucible remained empty. For these tests, both crucibles were heated with a constant current up to 300 °C (heating rate approx. 5 K/s). In Fig. 6, measurement data are shown. In the temperature range between 275 °C and 300 °C, differences between reference and sample curve occur. This can be seen in the inset of Fig. 6, in which the measured temperature difference between both heaters is plotted vs. the sample heater temperature. This difference originates from the melting of the sample. The acquired melting peak has a width of $\Delta T \approx 25$ K, see inset in Fig. 6. However, the melting point was determined to be 277 °C instead of 263 °C. Furthermore, one sees oscillations, interfering with the sensor signal. The power consumption for PCDSC structure is quite high, each of the heater requires 3.7 W at 330 °C (7.4 W together).

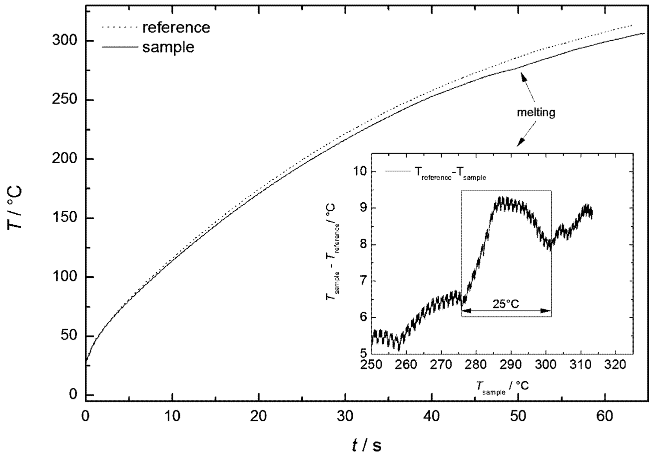

Fig. 6: Initial measurement of polyamide conducted in the LTCC-PCDSC chip. Temperature of the reference and sample during heating ramp. Inset: Temperature difference between sample and reference plotted vs. sample temperature.

The differences between the measurements in a commercial DSC apparatus and in the LTCC chip were attributed to an improper calibration of the chip and/or to a bad thermal contact between sample and crucible body. With this first measurement, we could show that detection of melting phenomena with PCDSC chip is – basically – possible. However, the results were very poor at this stage. The noise of the temperature difference signal originates from a consecutive alternating temperature measurement of both heaters. Therefore, no temperature data were available for one and the same time point. The attempt to calculate the temperature difference of both heaters based on these measurement data lead to a heavily noisy measurement signal. Moreover, the construction of the chip needed to be further optimized, especially the power compensation principle required better symmetry and better decoupling. Nevertheless, the results encouraged us to proceed with the LTCC-based DSC chip device, however, we decided to switch to the heat flux principle, since this requires only one furnace. The very promising final results (see below) confirmed this decision.

III. Dynamic Heat Flux DSC-Chip

In a heat flux DSC device (HFDSC), both sample and reference crucibles are heated with the same, usually constant heating rate in one single furnace (Fig. 7). During heating, the temperature of sample and reference are measured and the heat flux is calculated from the temperature difference between sample and reference using device-specific parameters (calorimetric constants) that include the heat capacity of the system and the thermal conductivity.

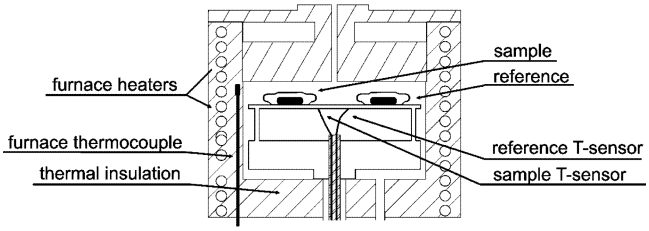

Fig. 7: Sketch of a typical dynamic heat flux DSC device (after [20]).

(1) Design of miniaturized ceramic HFDSC

It would have been challenging to miniaturize a heat flux DSC in a ceramic structure with one extended single heater (instead of a furnace) and two small elements for temperature measurement, since it is difficult to obtain a homogenous temperature distribution over the entire heater area. Therefore, heater and temperature sensors were arranged in a novel way. Instead of the usual horizontal embodiment of the mentioned elements, a vertical design was introduced. This is illustrated in Fig. 8. The heater is located exactly in the center of the device. Both temperature sensors are symmetrically arranged above and below the heater. While the sample temperature sensor is similar to the PCDSC chip covered by a thin layer (thin in comparison with the distance to the heater), the reference temperature sensor is covered by a thick ceramic block that is used as an internal reference. The working principle with the vertical arrangement was verified using a rotational symmetric FEM model with a simplified geometry. As in the above-presented simulations (Fig. 2), the material properties for LTCC ceramics and thick-film pastes were taken either from literature or were measured. Details on the modeling can be found in [24].

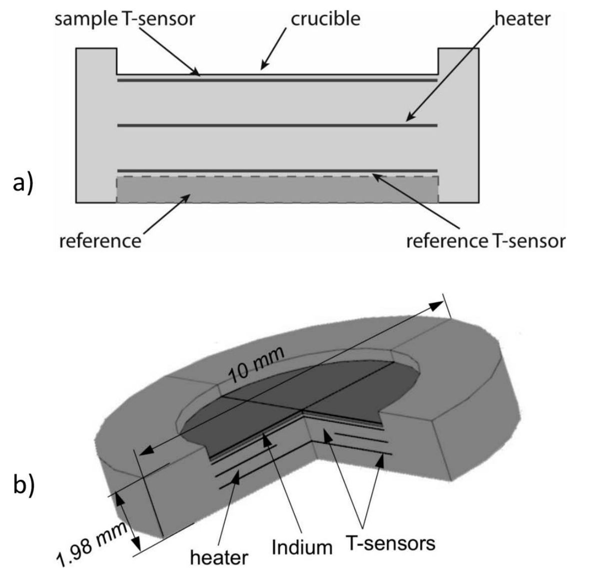

Fig. 8: Vertical arrangement of heater and temperature sensors in the novel heat flux DSC device (a). Rotational symmetric model for FEM simulations to estimate the effect (b).

To model a heating ramp, it was assumed that the crucible was filled with a film of homogenously distributed indium. An increased temperature difference between sample temperature sensor and reference temperature sensor results as long as the sample melts. Fig. 9 shows these temperature differences; approx. 20 mg indium (as a sample) was filled into the crucible. According to the modeling, one can expect a temperature difference of about 1 K when 20 mg of indium melt. This encouraging value should be sufficient to detect melting phenomena.

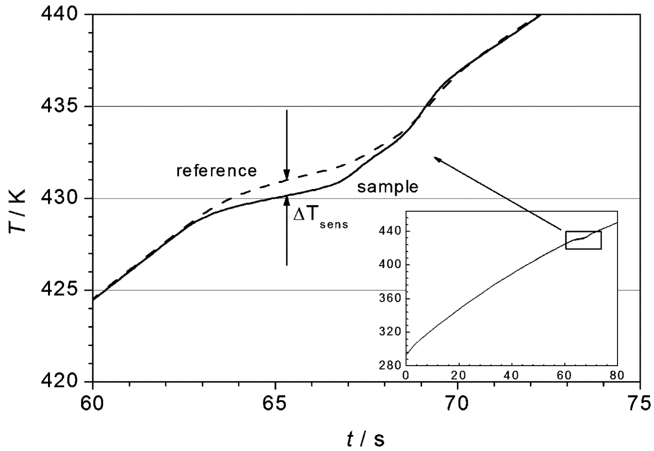

Fig. 9: Heating-up modeling results of the novel heat flux DSC (HFDSC) device, when the crucible contained 20 mg indium as a thin homogenous film.

The design of the heat flux DSC (HFDSC) device is shown in Fig. 10. Six LTCC layers cover the platinum heater from both sides. The two resistive platinum temperature sensors (for reference and sample, respectively) are located symmetrically above and below the heater. The sample temperature sensor is covered by a 50-μm-thin tape and the reference temperature sensor is covered by six tapes with a thickness of 135 μm each. These layers form an internal DSC reference. Another six tapes form a crucible itself, which just needs a small lid, or which just forms a seat for a standard DSC aluminum crucible. For precise resistance measurements, the heater as well as both temperature sensors are prepared for the four-wire measurement technique. The contact feeds are located on both sides of the structure.

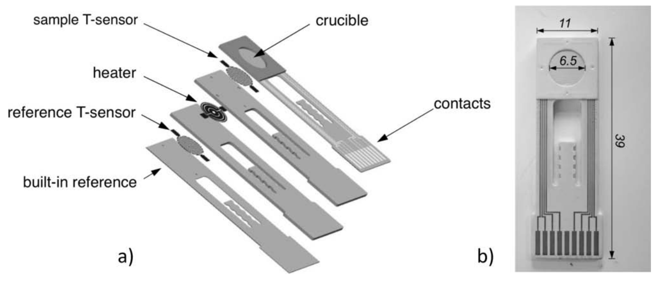

Fig. 10: Heat flux DSC device, fully manufactured in LTCC technology (a). For details, see text. Photograph of the manufactured DSC chip; dimensions in mm (b).

To thermally decouple DSC chip head and contact area, the ceramic in the middle between the contact feeds was removed by laser patterning of the green laminated sheets. The position of the contacts on both sides of the structure allows the use of a standard connector. Since the design of the chip head complies with one of a single crucible of the PCDSC chip, the heater design remains unaffected and a similar temperature distribution over the crucible was achieved. The mass of the structure, however, is reduced by 40 % compared to the previous design.

(2) *Characterization of heat flux DSC chip*

Fig. 10b shows a photograph of the HFDSC chip after firing. As in case of PCDSC, non-shrinkage HL800 tape was used. Heater and temperature sensors are made of platinum ink LP88 – 11 (Heraeus). For gold conductors and contacts TC 7102 (Heraeus) paste was applied. Since heater and temperature sensors are embodied as buried elements, the connection between them and contacts is realized by vias filled with gold paste (TC7101, Heraeus) in the low temperature contact area.

With dimensions of 11 mm × 39 mm and a thickness of 1.28 mm, the weight of the probe head of the HFDSC chip was reduced by about 20 % compared to single crucible of a PCDSC chip. This should improve the dynamic response of the system. Owing to the fact that the same materials were used for construction of HFDSC chip, the electrical properties of the heater and temperature sensors remained unchanged.

Similar to the PCDSC (Fig. 5), this version of the HFDSC chip exhibits non-radial temperature distribution in the crucible area caused by heat transportation through the beams. This effect has been minimized by reducing the beam width. Thus, the temperature field is more compact and moved from the top of the probe head towards its center. However, in both cases the temperature distribution in the crucible area is satisfactory with a deviation of ± 9.2 K at 500 °C.

For the very first tests with the vertical-designed HFDSC chip, indium was selected as a sample material (10.993 mg), since indium is one of the standard calibration materials for differential scanning calorimetry due to the reversibility of its phase transition and its well-known melting point at 156.5 °C. Prior to the measurement, the chip was calibrated as shown in [24]. The chip was mounted in a commercially available connector, the indium-filled aluminum crucible was added and a very simple hood covered both DSC chip and sample holder. Then the probe head was heated to above 200 °C (heating rate at indium melting point approximately 50 K/min). Owing to the single heater and to the compact design, the power consumption is drastically reduced, compared to the PCDSC chip. To achieve 330 °C only 4.02 W is required.

In Fig. 11, results from initial measurements obtained from the HFDSC chip compared to results from a commercial DSC apparatus (Mettler-Toledo 821e) are shown. For the HFDSC chip, the melting peak height appears lower than for the commercial DSC device (0.36 °C vs. 0.86 °C), however, in case of HFDSC chip the data were not additionally processed as it is standard for commercial DSC apparatuses. The small peak width suggests a good selectivity of the HFDSC chip. The difference in the absolute value of the peak temperature is a result of the missing individual calibration of the chip. Typically, one would use indium or another material with a well-defined melting temperature for an individual temperature calibration. Instead, here we used only a batch calibration (see above). However, it is noteworthy to say that for the initial tests, the presented result is more than satisfactory. More information about selectivity and repeatability are given in references [24, 25]. The present study is concerned with ceramic aspects of the chip development, whereas in [25], a first characterization of this device is given, leading to a calorimetric sensitivity at the indium melting point of 0.24 J/Ks. It depends linearly on temperature in the range of between 150 °C and 420 °C. The calorimetric sensitivity is independent of the sample mass up to an enthalpy of fusion of at least 750 mJ.

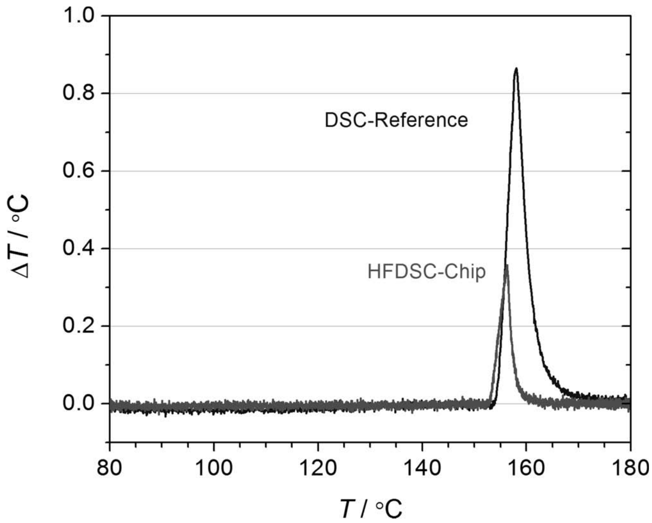

Fig. 11: Comparison of measurements made with commercial DSC apparatus and the DSC chip (sample: indium, 10.993 mg).

IV. Conclusions

The main developing steps of two novel miniaturized ceramic calorimeters entirely manufactured in low temperature co-fired ceramics (LTCC) technology are described. LTCC technology enabled the design of small and compact structures. With the power-compensated DSC chip, the melting point of polyamide was successfully identified. However, the working principle of the chip (power compensation with two independent heaters) does not seem to be the best solution for the selected thick-film technology and is hardly suitable for further miniaturization. The power requirement of the PCDSC chip is almost twice that for the HFDSC chip, making the latter more suitable for mobile applications. The novel vertical arrangement of temperature sensors and the integration of the reference into the chip structure allow the building of a compact chip that can be easily handled. First measurements with indium as a sample material showed that the HFDSC design could be successfully applied to detect melting points. Advantages for application compared to typical DSC apparatuses are the small dimensions and the relatively low costs since no expensive oven is required. Therefore, the novel LTCC DSC chip can be used for fast DSC analysis, especially in mobile devices. It is shown and has to be emphasized that without FEM modeling such a device could have never been realized.

Acknowledgments

This work was supported by German Federation of Industrial Research Associations (AiF), Grant No. 15435N. The authors thank Mrs U. Kuhn and Prof. V. Altstädt from University of Bayreuth, Dept. of Polymer Engineering for DSC measurements as well as Mr A. Müller and Prof. D. Brüggemann from Dept. of Technical Thermodynamics and Transport Processes for infrared camera support.

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