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Development of a Miniaturized Combined DSC and TGA Sensor

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Summary:
A miniaturized sensor with both, differential scanning calorimetry (DSC) and combined thermogravimetric analysis (TGA) functionality is presented. The ceramic sensor with integrated heater features high heating and cooling rates and enables the analysis of aggressive materials. The working principle based on the mass-dependent frequency change of the chip as a vibrating cantilever is described. The analysis of copper sulfate pentahydrate ($CuSO_4 \cdot 5\,H_2O$, an often-used reference substance) proves that DSC and TGA measurements can be carried out simultaneously under real conditions.

Keywords: DSC, Calorimetry, Thermogravimetry, Chip-DSC, LTCC.

Introduction

A differential scanning calorimeter (DSC) measures the difference in heat flow between a sample and a reference during a controlled temperature program. This important thermal analysis method is used to characterize phase changes, glass transitions, decomposition, recrystallisation or chemical reactions. Conventional DSC devices are complex apparatuses with an external furnace, which significantly increases the size and cost of such a device. As an alternative to conventional DSC devices, a miniaturized ceramic DSC chip with integrated heater was developed. The sensor is manufactured in Low Temperature Cofired Ceramics (LTCC) technology and is shown in Fig. 1. The small thermal mass of the sensor allows high heating and cooling rates and an excellent temperature control. In addition, materials can be analyzed that form aggressive gases and would damage or destroy conventional apparatuses. Detailed information about the design, manufacturing and proof of functionality is given in [1-4].

Integrating a Weighing Device

So far, the sample mass, which is required to obtain material parameters such as enthalpies or specific heat capacities, must be determined using an external laboratory balance. By integrating a weighing device directly into the DSC chip, not only the initial sample mass can be measured, but also small mass changes during thermal analysis. This development results in a completely new miniaturized device for thermogravimetric analysis (TGA) and combined simultaneous thermal analysis (STA), which enables more detailed correlation between gravimetric and caloric effects.

First steps of integrating a weighing device into the DSC chip were already described in [5]. On this basis, this contribution presents new and promising results with a combined DSC and TGA sensor.

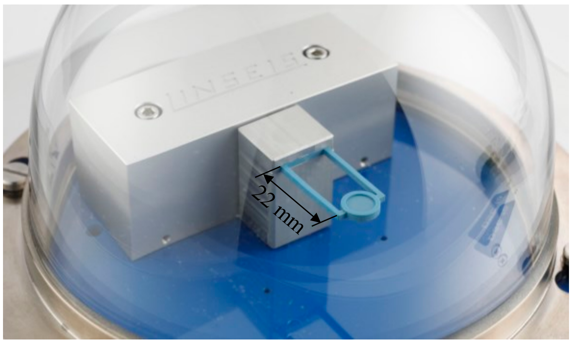

Fig. 1. Miniaturized ceramic differential scanning calorimeter chip.

Working Principle

The setup and working principle of the already existing DSC chip can be obtained from [1-4]. To introduce the functionality of the weighing device some theoretical considerations are briefly described. The working principle is based on the mass-dependent frequency change of a vibrating cantilever. As the sensor vibrates, the resonant frequency of the chip correlates with the mass load.

In the case of a periodic excitation with a continuous sinusoidal force, the chip oscillates at the excitation frequency. As the excitation frequency approaches the resonance frequency, the amplitude of oscillation increases and becomes maximum in the area of resonance. To obtain the resonance frequency, a frequency sweep is performed, and the maximum amplitude is evaluated. After calibrating the sensor, the frequency change can be converted into a mass change.

Measurement Results

Copper sulphate pentahydrate ($CuSO_4 \cdot 5\,H_2O$, an often-used reference substance) loses water of crystallization in three steps when heated [6]. As it shows a defined mass loss in three temperature ranges, dehydration of copper sulphate pentahydrate is measured to characterize the weighing functionality of the sensor chip.

Fig. 2 shows the simultaneously obtained DSC and TGA curves of three chip measurements in comparison with the TGA curve of a conventional TGA device. All measurements were taken at a heating rate of 10 K/min. The DSC curves illustrate the mass loss steps as endothermic peaks in the heat flux. The TGA curves are given as a percentage of the initial sample mass and show good reproducibility of the weighing functionality of the miniaturized chip. In addition, the onset temperatures of the mass loss steps obtained from the simultaneous DSC and TGA measurements agree very well. The comparison with the TGA curve of the conventional device demonstrates a good agreement in the height of the steps and proves the functionality of the mass measurement of the miniaturized DSC-TGA chip. A sensitivity of -1.18 Hz/mg is obtained by comparing with the reference measurement.

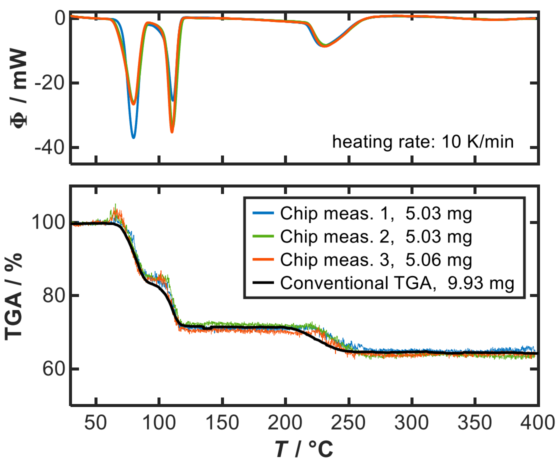

Fig. 2. Analysis of copper sulfate pentahydrate: heat flux measured with the DSC-TGA chip and TGA curve measured with the DSC-TGA chip in comparison with a conventional TGA. All measurements were performed at a heating rate of 10 K/min.

Conclusion

A miniaturized sensor with both, DSC functionality and combined TGA functionality was designed and manufactured. The principle of mass determination by obtaining the change in the resonant frequency of the sensor chip was proven for measurements under real circumstances. The simultaneous DSC and TGA measurements of the dehydration of copper sulphate pentahydrate show promising results and confirm the usability of the new combined chip.

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