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Determination of heat capacity by means of longitudinal guarded comparative calorimeter – Correction methods

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ABSTRACT

Even though Differential Scanning Calorimetry (DSC) is a well established method for the determination of specific heat capacity of various materials, there is also need for methods suitable for larger specimen sizes in the range of several cubic centimeters instead of micro liters. For phase change materials, i.e. a class of materials used for technical heat storage applications, or compounds which show size dependent thermophysical caloric properties below a critical specimen volume, e.g. subcooling effects, the larger specimen volumes are absolutely essential. The Longitudinal Guarded Heat Flow Method is a well-known steady state method to measure the thermal conductivity of medium sized solid samples. With a modification of the measurement procedure to a transient temperature step at the top and bottom end of the sample it is possible to determine the heat capacity of a specimen in a defined temperature interval. An apparent heat flux is determined during the transient heating phase. Numerical simulations of this new procedure are presented and discussed. The simulations indicate that, due to the transient nature of the technique, a correction in respect to the heat capacity of the reference specimens has to be applied to the measurement data. For this task a novel analytical method is provided. A correction factor is introduced which only depends on the geometry of the experimental setup. This analytical method is validated by numerical simulations. The results show good agreement and recommend the proposed method for the practical use.

1. Introduction

Thermal energy storage with phase change materials (PCM) gained a lot of interest in the last 20 years [1]. The main advantage of PCM is their ability to store a large amount of heat in a small temperature interval. Therefore, a main aspect in PCM research is the determination of the heat storage capacity. In many cases there is considerable uncertainty in the values given by the manufacturers [2]. For the characterization of thermal properties of materials special attention to the sample size is required. It has to be representative for the bulk material when composites are analyzed. For example thermal conductivity enhancement of PCM is often realized by adding expanded graphite [3–5]. The macroscopic pore size of these graphite composites can be in the order of 100 μm, especially for low relative graphite densities. Therefore the specimen size should be at least several cm^3 to be representative. But also properties of homogeneous materials can be size dependent. For example some phase change materials like salt hydrates or water show an increase of subcooling when the specimen size is decreased [6–8]. Therefore the specimen size should be typical for the application [9]. For small sample sizes differential scanning calorimetry is the method of choice. Large specimen sizes, like PCM systems used for building applications are investigated in test rooms. For medium size components, like macro encapsulated PCM and building components containing PCM, there is a technological gap in metrology up to now.

The Guarded-Comparative-Longitudinal Heat Flow Technique (LHFT) is a steady-state method to measure thermal conductivity of medium sized solid samples. The technique is also known as Cut-Bar-Method and Divided Bar Method. Fig. 1 shows a schematic diagram of the technique. The experimental method is described in detail in ASTM E1225-99 [10]. For thermal conductivity measurement with the LHFT a temperature gradient is established in a stack consisting of one specimen bar between two reference bars so that heat flows axially through the bars. Two temperature sensors in each reference bar and the sample bar measure the temperature difference ΔT at a specified distance Δz.

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Nomenclature

Roman symbols

a	thermal diffusivity ($m^2 \cdot s^{-1}$)
B	correction term (−)
Bi	biot number (−)
C	coefficient of the boundary value problem (−)
c	specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)
d	relative deviation (%)
k	number of terms (−)
L	latent heat ($kJ \cdot kg^{-1}$)
l	specimen length (m)
m	mass (kg)
q	heat ($J \cdot m^{-2}$)
$\dot{q}$	heat flux ($W \cdot m^{-2}$)
R	reference height (m)
T	temperature (°C)
t	time (s)
w	peak width (K)
z	vertical position in the stack (m)

Greek symbols

λ	thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
μ	eigenvalue of the boundary value problem (−)
ρ	density ($kg \cdot m^{-3}$)
τ	time (s)

Subscripts

*	stationary conditions used
+	dimensionless
0	initial value
c	corrected
e	empty
i	sensor position
m	melting
n	summation index
pcm	phase change material
r	reference bar
s	sample bar
u	end value

Abbreviations

DSC	differential scanning calorimetry
LHFT	longitudinal heat flow technique
PCM	phase change materials
PEEK	polyether ether ketone

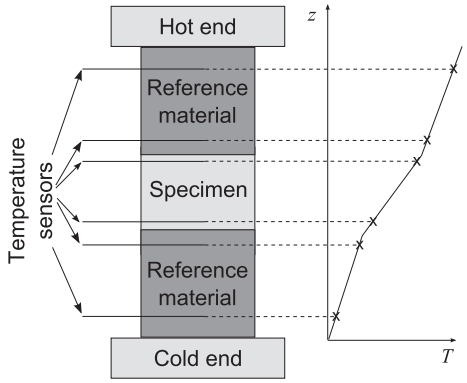

Fig. 1. Schematic diagram of the longitudinal heat flow meter setup for thermal conductivity measurements and typical temperature profile inside the stack.

The surrounding of the stack is thermally well insulated. Therefore the heat flow is quasi-one dimensional and in system steady state the heat flux $\dot{q}$ through the stack can be calculated using a difference quotient in Fourier's law:

$$\dot{q} = -\lambda \frac{\Delta T}{\Delta z} \tag{1}$$

where λ is the thermal conductivity. The heat flow through the reference bars is the same as through the sample and therefore the thermal conductivity of the specimen λ_s is calculated by

$$\lambda_s = \lambda_r \frac{\Delta T_r}{\Delta T_s} \frac{\Delta z_s}{\Delta z_r} \tag{2}$$

with the thermal conductivity of the reference material λ_r, the temperature difference in the specimen ΔT_s and reference ΔT_r and the sensor distance in the specimen Δz_s and reference Δz_r.

With a modification of the measurement procedure to a transient temperature step at the top and bottom end of the stack it is possible to measure the heat flowing into the test specimen in the defined temperature interval. Antriasian and Beardsmore [11] used the setup to measure specific heat of rock material. They measured the temperature difference in the reference bars during a temperature step program and calculated the heat flux into the sample using Fourier's law. During this program the system is no longer in steady state, so the calculation of heat flux with Eq. (1) causes incorrect values. They did a calibration by measuring specimens with known thermal properties. From the calibration measurements they derived a correction factor which compensates the heat capacity of the apparatus. Farnam et al. [12] used this modified technique to measure latent heat in freeze and thaw experiments in mortar.

2. Computational setup

The deviation of the experimental derived values by applying Eq. (1) from the true values are quantified by numerical simulations. For the simulations the finite element solution environment FlexPDE [13] was used. For the investigations in this paper one temperature step is chosen. Fig. 2 shows a schematic of the calorimetric setup. On the right hand side the temperature profile in the stack at different times is shown. Starting at isothermal conditions in the whole stack $T_0 = 0$ C at $t_0 = 0$ the temperature at the heaters is instantly changed to a higher value $T_u = 30$ °C. For t_1 and t_2 snapshots of the temperature profile in the transient state of the measurement are shown. During these states the profile is nonlinear. At $t_3 \rightarrow \infty$ the system again reached thermal equilibrium at T_u.

Ignoring lateral heat loss and assuming that all bars have the same cross sectional area, the problem was simplified to one-dimensional heat conduction. Because of the symmetry of the system, only half of the setup has to be considered. The simulation setup is shown in Fig. 3 and the material properties used are listed in Table 1. The specimen and the reference have the same length $l = R = [0.04]$ m. The dimensionless sensor positions $z_i^+ = \frac{z_i}{R}$ inside the specimen are 1/4 and 3/4.