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Correction of the enthalpy–temperature curve of phase change materials obtained from the T-History method based on a transient heat conduction model

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ABSTRACT

Utilizing the latent heat of materials undergoing phase transitions, or so called phase change materials (PCMs), for thermal energy storage offers higher storage densities compared to purely sensible thermal energy storages. For evaluating different PCMs the T-History method has often been applied by researchers in order to determine the characteristic enthalpy versus temperature curves. In previous research many different T-History setups are described where the sample holder is insulated. The intention is to decrease internal temperature gradients inside the sample holder with PCM. However, in the mathematical model for evaluating the enthalpy curve of the PCM based on the measured temperature response, the thermal mass of the insulation around the sample holder has been neglected.

In this study, a one dimensional numerical transient heat transfer model is used to show that neglecting the insulation thermal mass leads to a systematic error on the obtained enthalpy versus temperature curves. The error is caused by deviations in the transient heat flows for reference and PCM sample when both are cooled down or heated, respectively. These deviations can be corrected by introducing a correction factor.

1. Introduction

Thermal energy storage systems have the potential for bridging the gap between intermittently available renewable energy sources and energy demand. Compared to purely sensible energy storage concepts, the use of the latent heat of melting and solidification by so called phase change materials (PCMs) offers considerably larger energy storage densities. Therefore PCMs have gained considerable attention in the last decades by researchers [1–3]. Depending on the temperature range, a vast amount of different material classes have been investigated [4]. Accurate and representative measurement of the heat stored and released within the phase change temperature range is of major importance when evaluating the suitability of a PCM for thermal energy storage applications. In the literature these are usually presented in terms of an enthalpy versus temperature curve.

An overview of different experimental thermal analysis methods for PCMs can be found in Cabeza et al. [5]. For small (milligram range) sample sizes, the intercomparability of results from different commercially available differential scanning calorimetry (DSC) instruments has been recently improved by employing standardized measurements after round robin tests [6,7]. However, for heterogeneous materials, such as salt-hydrates with nucleating agents, sample sizes applied by commercial DSC instruments may not be representative for the bulk material, since supercooling may be artificially enhanced when the sample size is chosen as too small [8].

As an alternative to DSC, the so called T-History method utilizes sample sizes typically above 10 g and has been applied widely by researchers since its introduction by Zhang et al. [9] over a decade ago. A first review of the method is given by Solé et al. [10]. In the review it is pointed out that the T-History method has been applied with many different experimental setups and that the enthalpy–temperature curve has been calculated with different data evaluation models depending on the author. However, the consequences of these differences on the enthalpy results have usually not been discussed so far. An agreement among researchers on the experimental setup and the mathematical model is therefore needed, in order to make the results from the T-History

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Nomenclature

a	thermal diffusivity [m^2/s]
c_p	specific heat capacity [J/kg K]
e	correction factor [–]
H_L	latent heat [J/kg]
h	specific enthalpy [J kg]
L	characteristic length [m]
Q	heat flow [W]
q	heat flow density [W/m^2]
R_{th}	thermal resistance [K/W]
r	radius [m]
T	temperature [K]
t	time [s]
w	phase change temperature range [K]

Greek letters

α	heat transfer coefficient [W/m^2 K]
λ	thermal conductivity [W/m K]
ρ	density [kg/m]

Subscripts

amb	ambient
c	center
ins	insulation
PCM	sample (phase change material)
ref	reference
t	sample holder tube
w	sample holder tube wall

method intercomparable. This is especially true since all mathematical models for the method so far rely on simplifications, such as the assumption of a lumped capacity for the PCM sample holders.

Recently, works were published which have started to address these aspects. D'Avignon and Kummert [11] discussed the application of different mathematical models and data evaluation approaches present in the literature. They recommend to use the model introduced by Marin et al. [12] as the currently best representation of the T-History method available. Despite the recommendation, the authors point out that the model was adjusted to absolute temperature intervals in order to display supercooling in the enthalpy versus temperature curve. However, this is likely a wrong representation since the model does not take the supercooling effect into account rigorously. It should be noted that when results with supercooling are presented in previous publications, usually no details on the data evaluation method is provided.

Mazo et al. [13] studied for the first time theoretically the error of assuming the sample to have an uniform temperature based on a 1-D conduction model of a cylindrical PCM sample holder without insulation. Since temperature gradients are present in the PCM sample holder, especially during phase change, the assumption of a uniform temperature leads to errors in the resulting enthalpy versus temperature curve. They conclude that the lumped capacity assumption has to be critically assessed in future experiments and proposed a more restrictive criteria based on the Biot number.

The majority of recent T-History setups include an insulation around the sample holder to reduce thermal gradients inside the sample container. However, the thermal mass of the insulation has never been considered before in any mathematical model when calculating the enthalpy versus temperature curve of the PCM.

A general challenge for any experimental method is therefore to reduce systematic deviations from the true material properties caused by the measurement method and the underlying mathematical model. A calibration of the experimental setup with well-known materials is always recommended. Rathgeber et al. [14] addressed this aspect experimentally for the first time. They presented a calibration method of their T-History experimental setup where two different calibration factors were used. The calibration factors were obtained from measurements of Copper and Indium for the sensible and latent region respectively. These materials were chosen because of their well-documented material properties. The enthalpy versus temperature curves were evaluated from T-History measurements for three different PCMs. The corrected results showed better agreement between the T-History and DSC measurements than before the calibration.

The aim of this work is to further develop the T-History method for characterizing large PCM samples. We discuss this issue first by giving a discussion of the main assumptions behind the T-History method. Then we show based on a 1-D transient heat conduction simulation the consequences of neglecting the insulation on the resulting enthalpy–temperature curves. Finally, a proposal is given on how the enthalpy–temperature curves can be corrected accordingly. We believe that our work offers a part of the theoretical background on why a correction of the enthalpy results are practically needed with insulated sample holders, as it has been experimentally shown by Rathgeber et al. [14].

2. The T-History method in the literature

Fig. 1 shows a sketch of a typical T-History experimental setup. A PCM sample and reference are placed in identical sample holders respectively. Both materials are brought to thermal equilibrium in a temperature controlled environment, where the PCM sample is at initially homogeneous liquid state.

When the sample and reference are in equilibrium with the surrounding environment, they are subjected to a sudden drop of the ambient temperature. The ambient temperature is held constant and the cooling curve (temperature over time) is recorded for both sample and reference. The first fundamental assumption of the T-History method is that the overall heat flow Q [W] from the sample to the ambient and from the reference to the ambient are equal for the same sample and reference temperature T [K]. This means that the overall heat transfer coefficient, or the thermal resistance R_{th} [K/W] of the sample holder, are assumed to be equal for the same temperature difference $T_{ref/PCM} - T_{amb}$.

$$Q_{ref}(T_{ref}) = Q_{PCM}(T_{PCM}) = \frac{1}{R_{th}(T_{ref/PCM})}(T_{ref/PCM} - T_{amb}) \tag{1}$$

The second fundamental assumption of the T-History method is that negligible temperature gradients reside inside the sample and reference holders. For uninsulated sample holders this assumption has been justified in the literature by keeping the Biot number criteria below 0.1, which was first introduced by Zhang et al. [9]:

$$Bi = \frac{\alpha \cdot L}{\lambda} < 0.1 \tag{2}$$

In Eq. (2), α [W/(m^2 K)] is the heat transfer coefficient of the sample holder to the ambient, L [m] a characteristic length of the sample holder tube and λ [W/(m K)] the thermal conductivity of the PCM or reference. This means that a lumped capacitance model