Materials and Design 95 (2016) 198–203

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

# A Computer Aided Cooling Curve Analysis method to study phase change materials for thermal energy storage applications

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ARTICLE INFO

*Article history:*
Received 6 August 2015
Received in revised form 3 January 2016
Accepted 13 January 2016
Available online 21 January 2016

*Keywords:*
Thermal energy storage
PCMs
CACCA

ABSTRACT

The suitability of a simple Computer Aided Cooling Curve Analysis (CACCA) technique for characterizing thermal energy storage phase change materials (PCM) was proposed in the present work. Two modes of CACCA, namely, Newtonian and Fourier techniques were used to predict the phase transition temperatures, the latent heat of fusion and thermal diffusivities of PCMs. Solidification of potassium nitrate and zinc–8% aluminium alloy (ZA8) was studied using CACCA method. These PCMs were chosen to demonstrate the ability of the proposed technique to characterize PCMs freezing at a single temperature as well as over a range of temperatures. CACCA method showed that potassium nitrate and ZA8 are suitable candidate materials for TES applications operating at 300–350 °C and 350–450 °C respectively.



## 1. Introduction

In recent years, thermal energy storage (TES) technologies have significantly improved the sustainability of various power plants. The development of these technologies is considered to be as important as developing new energy sources. A large number of applications have been identified in power sectors, medicine and the food industry. As sensible heat storage systems have poor energy densities, the prime focus is now on the development of latent heat storage systems using phase change materials (PCM). For successful development of TES studies, an accurate database on specific heat capacities, phase transition temperatures and the corresponding enthalpies is required.

Thermal analysis (TA) is the most suitable technique to characterize TES materials. In this technique, the substance is subjected to a programmed and controlled temperature environment and the physical property of a substance is measured as a function of temperature. TA techniques are classified on the basis of the physical property being measured. For example, techniques like Thermogravimetry, Evolved gas analysis and Thermoparticulate analysis measure the change in sample mass to study its thermal behaviour. Cooling curve analysis and Differential thermal analysis measure temperature change while the change in enthalpy is measured in differential scanning calorimetry. The dimensional changes in a sample are measured using Thermodilatometry. Thermosonimetry and Thermoacoustimetry are used to analyse acoustic characteristics while Thermoptometry, Thermoelectrometry and Thermomagnetometry are used for optical, electrical and magnetic characteristics respectively.

Characterization of TES materials to obtain information on their specific heat and latent heat has been solely carried out using differential scanning calorimetry by most of the researchers. Limitations of this technique have surfaced in recent years diminishing its utility. Major limitation of differential scanning calorimetry technique used to determine relevant properties is the size of the sample, in the order of milligrammes. The size of the sample is too small to represent an inhomogeneous material. In materials like composites where attaining homogeneity is a difficult task, the measured values do not represent the material property but solely reflect the properties of the specific sample. In the current scenario where researchers design new composite materials for superior TES functionalities, the differential scanning calorimetry technique remains flawed.

The differential scanning calorimetry results are also influenced by the heating and cooling rates. Higher rates develop thermal gradients in the sample. This is one reason why a material, expected to solidify isothermally, is observed to freeze over a temperature interval in differential scanning calorimetry curves. Lower heating/cooling rates can significantly reduce the base-width of the peaks in the differential scanning calorimetry causing a low signal to noise ratio inflating the inaccuracies in the measured values. Another problem that arises due to small sample size is an overestimate of the magnitude of subcooling. Smaller the sample, more is the tendency to supercool i.e. to temporarily remain as liquid below the normal freezing temperature. Thus the heat of fusion values measured using differential scanning calorimetry is lower compared to that observed in large samples, as the loss in heat of fusion due to considerable subcooling remains unaccounted in differential scanning calorimetry. It is generally known that with considerably larger sample sizes, the transition temperatures obtained from the differential scanning calorimetry method are often lower to the values observed in other techniques. These inaccuracies pile up and prove to be challenging when designing a TES system on a large scale. The effect of sample size and heating–cooling rates on specific heat

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http://dx.doi.org/10.1016/j.matdes.2016.01.053
0264-1275/

**Nomenclature**

| | |
|---|---|
| Q | Heat transferred, kJ |
| M | Mass of the test sample, kg |
| $C_p$ | Specific heat capacity of test sample at constant pressure, kJ/kg·K |
| $C_v$ | Specific heat capacity of test sample at constant volume, kJ/kg·K |
| T | Temperature of sample, °C |
| $T_o$ | Ambient temperature, °C |
| t | Time, s |
| A | Surface area for heat transfer, $m^2$ |
| $Z_c$ | Zero Curve or Baseline |
| $\alpha$ | Thermal diffusivity, $m^2/s$ |
| $\lambda$ | Thermal conductivity, W/m K |
| $\rho$ | Material density, $kg/m^3$ |
| L | Latent heat of fusion, kJ/kg |
| U | Overall heat transfer coefficient, $W/m^2$ K |

capacity values obtained from differential scanning calorimetry measurements, and various aspects in calibration of differential scanning calorimetry instrument both in dynamic and step modes were discussed by Mehling and Cabeza [1], which throws more light on the effectiveness of differential scanning calorimetry measurements.

Another calorimetric method suitable for TES studies is the T-history method, where large samples can be analysed. This technique overcomes the limitations of differential scanning calorimetry technique. Here, a reference material of known properties is heated/cooled over the concerned temperature range along with the sample (PCM). The variations in their temperature history are analysed to measure relevant properties like specific heat and latent heat. This method was first introduced by Yinping et al. [2], and was later improved by calculating heat capacities as a function of temperature by Marin et al. [3]. A collection of various methods similar to the T-history method was discussed and reviewed by Sole et al. [4].

T-history method has been successfully used to study various low temperature PCMs (organic PCMs). This technique has serious limitations that diminish its utility for high temperature studies. For high temperature studies, the use of water and low carbon organic compounds as the reference material is not possible as they vaporize easily (at temperatures above 150 °C). Low temperature melting metals, alloys (alloys of Ga, In.) and Heat transfer fluids (like Liquid Na, NaK) are very expensive. High carbon organic compounds are suitable candidates but they are highly inflammable and show a rise in melting point with increase in carbon number. In addition to this, container material needs to be selected judiciously. Chemical interactions such as corrosion, need to be studied for every pair of PCM-Container material over wide temperature range. A detailed database for this purpose is not available at present. Ceramic containers are ideal for these conditions. This technique requires a cylindrical container with a length to diameter ratio greater than 16. Manufacturing ceramic cylinders of such dimensions with thin wall thickness to ensure higher heat transfer rates are difficult. A survey of the literature suggests that all reference materials are suitable only over a certain temperature range and developing a standard reference material suitable for a wide temperature range of 200–1000 °C is difficult. The use of borosilicate and quartz container eliminates such chemical interactions but they are brittle and are prone to failure at higher temperatures. Overcoming these obstructions with expensive materials and sophisticated system design makes the technique a very complex and not a cost-effective alternative to differential scanning calorimetry. These factors discussed above convincingly advocate for a novel technique to determine heat capacity and heat of fusion of energy storage materials over a wide range of temperatures.

In the present investigation, a novel TA technique based on Computer Aided Cooling Curve Analysis (CACCA) to characterize TES materials is proposed. The method records the temperature changes in the sample as it cools through various phase transformations. This technique can be used for quantitative measurement of thermophysical and thermodynamic characteristics of the investigated material. Information on latent heat of solidification, phase transition temperatures, solid fraction, amounts and types of phases, loss in enthalpy due to undercooling were obtained. The method has an edge over the techniques such as differential scanning calorimetry and T-history technique as it is simple and inexpensive and yields consistent results. A salt and a metallic PCM (alloy) were analysed to demonstrate the suitability of this technique in studying PCMs solidifying both at a single temperature as well as over a range of temperatures. Metals being an effective alternative to salts in TES applications [5–9] are also discussed in the present work.

### 1.1. Theoretical background

CACCA can be classified into Newtonian & Fourier techniques. The Newtonian technique does not take into account the local temperature gradients developed during solidification. On the other hand, the Fourier technique incorporates the effect of thermal gradients during solidification. This comparison between the Fourier and Newtonian methods indicates that their predictions are appreciably different. The Newtonian method of CACCA uses basically one thermocouple placed in the centre of the test sample while the Fourier technique uses at least two thermocouples with one offset from the centre.

The primary information obtained from cooling curves is the phase transition temperature. Transition temperatures appear as a kink followed by a considerable change in slope in the first derivative curve. The first derivative curve is the most relevant tool in CACCA. The increase in the slope can be attributed to nucleation while its drop would represent cooling or remelting of the sample. Eutectic transitions appear as straight lines while undercooling appears as loops.

### 1.2. Newtonian technique

Here, the sample can be considered as “the lumped thermal system” as the temperature distribution is assumed to be uniform throughout the test sample. Further, the sensible specific heat for the sample is

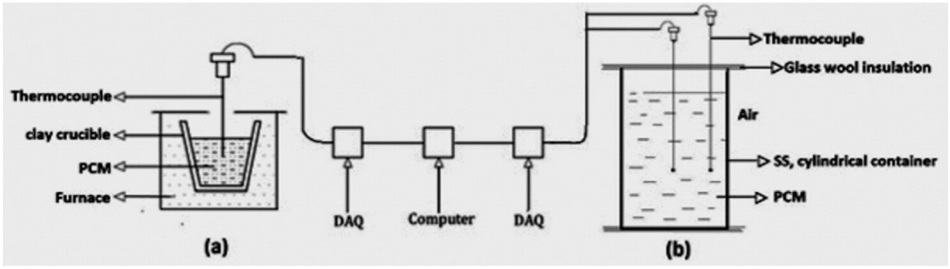


**Fig. 1.** Schematic sketch of CACCA setup (a) Newtonian method, (b) Fourier method.