PCM-GRAHITÉ COMPOSITES FOR HIGH TEMPERATURE THERMAL ENERGY STORAGE

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1. BACKGROUND

Storage systems based on Phase Change Materials (PCMs) with solid-liquid phase transition are considered to be an efficient alternative to sensible thermal storage systems. From an energy efficiency point of view, PCM storage systems have the advantage that they operate with a small temperature difference between charging and discharging. Furthermore, these storages have high energy densities compared to sensible heat storages assuming such energy efficient operation. However, there are heat transfer limitations on the storage design due to the low thermal conductivity of PCMs. These limitations lead to a low charging and discharging power of the storage. Various methods have been proposed to enhance the heat transfer of the poorly conducting PCMs, such as additional fin structures or dispersed particles with a high thermal conductivity, as well as microencapsulated PCMs [Zalba 2003]. Another major approach is the use of composite latent heat storage materials (CLHSM). Here, the properties of a high latent heat of the PCM and the good thermal conductivity of an additive are combined. For low temperature applications, paraffin-graphite CLHSM have been reported [Py 2001, Marín, 2005].

Our ongoing research focuses on high temperature storage designs for industrial process heat utilization and solar power generation using direct steam technology in parabolic trough plants. For both applications, the heat transfer fluid is water-steam. The concept is as follows: During the charging period, heat from the condensing steam is transferred to the melting PCM; during the discharging process, heat from the solidifying PCM is used to generate steam. The analysis of this concept presents another paper at this conference [Buschle 2006]. For the discussed applications, this isothermal storage concept requires PCMs with a melting temperature in the range from 130 to 320°C [Tamme 2005]. PCM considered for this temperature range are mainly anhydrous salts. We studied CLHSM previously using alkali nitrate salts as PCMs and graphite as a heat transfer enhancer [do Couto Aktay 2005].

The target of the effective thermal conductivity of the CLHSM is in the range from 5 to 15 W/mK. This range results from the charging and discharging power requirement of the storage system [Buschle 2006]. There is a variety of potential preparation routes for the CLHSM and these routes have a decisive impact on the interconnectivity of the graphite. Generally a highly interconnected graphite matrix is desirable in order to achieve a high effective thermal conductivity.

Previously, CLHSM using KNO3-NaNO3 and graphite were prepared by uniaxial cold and warm compression [do Couto Aktay 2005]. Effective thermal conductivities were measured by a comparative apparatus. Results showed that the effective thermal conductivity decreased with temperature with no major change of the conductivity values above the melting temperature of the PCM. In comparison with the single PCM, composites had conductivities about three to five times higher [do Couto Aktay 2005].

Work in this paper presents characterization results of CLHSM prepared by high-force compression and infiltration. For the characterization of the composites, the laser-flash method is utilized. This method allows for a faster characterization compared to the comparative method.
2. PREPARATION OF THE COMPOSITE LATENT HEAT STORAGE MATERIALS

As a PCM, we select the equimolar composition of potassium nitrate (KNO3) and sodium nitrate (NaNO3) with a melting temperature of about 220°C (K-NaNO3-eu). We prepared the eutectic mixture using technical salts:

- KNO3: purity >99.0%, others are 0.015-0.030% Cl, <0.05% Na, 0.03% Ca, <10 ppm heavy metals, <0.08% anticaking agent, <0.05% water insolubles, 0.04% moisture
- NaNO3: purity >98%, others are <0.48% Cl, 0.15% SO4, 0.02% NO2, <5 ppm Fe, <1 ppm Cu, <1 ppm Cr, <5 ppm Pb, <0.1 ppm As, 0.1% insolubles, 0.1% moisture

For some CLHSM extra pure KNO3 and NaNO3 from Merck were used (Ordering Number KNO3: 1.05061.1000, NaNO3: 1.06535.1000).

The graphite crystal has the structure of stacked parallel layer planes. Within each layer plane, the bond is covalent and has a high strength compared to the weak van der Waals bonds between the planes. This crystal structure results in a considerable anisotropy. Hence, the material properties may vary considerably when measured within the plane or perpendicular to the plane [Pierson 1993].

This work uses different graphite types to form the CLHSM. Figure 1 summarizes these types. Expanded graphite (EG) was produced from natural graphite by intercalation, followed by exfoliation by heating rapidly to a high temperature. The resulting EG presents a worm-like or vermicular structure. For some CLHSM, ground EG with a d50 value of 500 µm was used. This material is commercially available from SGL Technologies GmbH (SGL) as GFG500 under the trade name Conductograph®. In addition, EG can be compressed to foils or plates. Compressed expanded graphite (CEG) has a number of applications such as high-surface materials and high temperature seals and gaskets [Pierson 1993]. In this work, porous CEG plates with a low density of 0.07 g/cm³ were infiltrated with K-NaNO3-eu.

Table 1 gives an overview of the CLHSM. SGL prepared all graphite types and CLHSM. The German Aerospace Center (DLR) carried out the characterization of the CLHSM.

We determined the composition in two steps. Firstly, the weight of part of the specimen was measured. Secondly, the salt was removed by dissolving in water and the weight of the residual graphite was determined. For the compressed samples, the composition was spatially heterogeneous and the described method could not be utilized. For these samples the composition by weight was determined during the preparation process. In order to specify the density of the samples, the geometry and weight of the laser flash discs were measured. We determined the volumetric composition from the sample density and the salt-graphite mass fraction, as well as the theoretical densities of K-NaNO3-eu \( \rho_s = 2.18 \) g/cm³ and graphite \( \rho_g = 2.26 \) g/cm³ [Pierson 1993]. The density of K-NaNO3-eu is an average value from KNO3 and NaNO3 [Schinke 1960]. Table 1 gathers the results of these characterizations.
Table 1: Overview of CLHSM. Densities and Volumetric Compositions were obtained from the Laser-Flash Discs.

<table>
<thead>
<tr>
<th>Preparation route</th>
<th>Graphite type</th>
<th>Salt grade</th>
<th>Mass</th>
<th>Thermal Cycling</th>
<th>Density [g/cm³]</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Salt</td>
<td></td>
<td>Salt vₜ</td>
<td>Graphite vₜ</td>
</tr>
<tr>
<td>Compression</td>
<td>Technical</td>
<td></td>
<td>90%</td>
<td>Before</td>
<td>2.0</td>
<td>83%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
<td>After</td>
<td>1.6</td>
<td>66%</td>
</tr>
<tr>
<td></td>
<td>Technical</td>
<td></td>
<td>80%</td>
<td>Before</td>
<td>1.9</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20%</td>
<td>After</td>
<td>2.0</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>Technical</td>
<td></td>
<td>70%</td>
<td>Before</td>
<td>2.1</td>
<td>67%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30%</td>
<td>After</td>
<td>1.9</td>
<td>61%</td>
</tr>
<tr>
<td>Infiltration</td>
<td>Extra pure</td>
<td></td>
<td>70%</td>
<td>Before</td>
<td>1.8</td>
<td>78%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30%</td>
<td>After</td>
<td>1.4</td>
<td>61%</td>
</tr>
<tr>
<td>Infiltration</td>
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<td>95%</td>
<td>Before</td>
<td>1.8</td>
<td>78%</td>
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<td></td>
<td></td>
<td></td>
<td>5%</td>
<td>After</td>
<td>1.4</td>
<td>61%</td>
</tr>
</tbody>
</table>

2.1 Preparation of Composites by Compression using GFG

For the compression route, powder mixtures of GFG500 and K-NaNO₃-eu were fabricated. The graphite content of the mixtures was 10, 20 and 30% by weight, respectively. Then this powder mixture was filled in a die and compressed at room temperature. The size of the compressed blocks was about 150 x 130 x 80 mm³.

2.2 Preparation of Composites by Infiltration using NG and EG

Fills of NG flakes and porous CEG plates were infiltrated with molten K-NaNO₃-eu using vacuum pressure infiltration. For the infiltration, the NG fills and the CEG plates, respectively, were installed in a metal container and submerged with the molten PCM. Then the container was installed in an autoclave heated to 260°C that was first evacuated for 10 min to a residual pressure below 100 mbar and then pressurized with argon gas for 10 min to force the PCM into the pores of the NG fills and CEG plates. The argon pressure was 7 bar for the NG fill infiltration and 5 bar for the porous CEG plate infiltration. After cooling down and solidification of the PCM, the infiltrated NG fill was taken out of the container and the excess salt that had not infiltrated the pores of the fill was removed. In contrast, the infiltrated CEG plates were removed from the container before solidification of the salt mixture.

3. EXPERIMENTAL PROCEDURE OF THERMOPHYSICAL CHARACTERIZATION

3.1 Thermal Cycling

For thermal storage operation, the CLHSM need to undergo frequent thermal cycles of melting and solidification of the PCM. Previous work illustrated that cycling alters the properties of CLHSM [do Couto Aktay 2005]. In detail, scanning electron micrographs showed differences in the microstructure. In addition, thermal conductivity measurements showed lower values for the cycled samples [do Couto Aktay 2005]. Hence, in this work the CLHSM were thermally cycled in order to assess the segregation, form stability, irreversible expansion and mass loss of the samples. We carried out thermal cycling of the CLHSM in evaporating dishes and stainless steel cylinders with one open end. For the steel cylinder, the sample dimensions (40 mm diameter, height of 40 mm) matched the cylinder diameter closely. All samples were cycled using ten times the following segments: isothermal (170°C, 60 minutes), heating (170-270°C, 60 minutes), isothermal (270°C, 60 minutes) and cooling (270-170°C, 60 minutes). For the characterization of the CLHSM the laser flash method was utilized.

3.2 Determination of the Thermal Conductivity using the Laser-Flash Method

This method, first described by Parker et al. [Parker 1961, Vozár 2003/2004], is a transient technique whereby the front face of a sample is heated by a short laser pulse. The temperature rise on the rear surface of the specimen is measured over time and used to calculate the thermal diffusivity \(a\). Major advantages of the laser-flash method include the broad temperature and thermal diffusivity range. Furthermore, measurement periods are short compared to steady state methods. On the other hand, this method requires additionally accurate data of the density \(\rho\) and the specific heat \(c_p\) in order to calculate the thermal conductivity \(\lambda\) (Equation 1). For the composites, it is necessary to
calculate effective $c_p$ and $\rho$ values. The Equations 2 and 3 define the effective heat capacity $c_{p,\text{eff}}$ and density $\rho_{\text{eff}}$ of the composite [Taylor 1983], where $v$ is the volume fraction (see Table 1) and the indices $s$ and $g$ represent salt and graphite, respectively. The pores do not impact decisively on these effective properties. Hence, for the pores the terms in the two equations were assumed zero.

$$\lambda = a \cdot c_{p,\text{eff}} \cdot \rho_{\text{eff}}$$

(1)

$$\rho_{\text{eff}} = \rho_s \cdot v_s + \rho_g \cdot v_g$$

(2)

$$c_{p,\text{eff}} = \frac{\rho_s \cdot c_{p,s} \cdot v_s + \rho_g \cdot c_{p,g} \cdot v_g}{\rho_{\text{eff}}}$$

(3)

For the heat capacity of graphite and K-NaNO3-eu, temperature dependent data were utilized [Pierson 1993]. KNaNO3-eu data were averaged values from KNO3 and NaNO3 [Carling 1983]. At the current stage of research, dilatometer measurements of the samples were not available. Therefore, the calculations assumed densities at room temperature ($\rho_s = 2.18$ g/cm$^3$ and $\rho_g = 2.26$ g/cm$^3$). Laser-flash measurements were carried out with a LFA457 from Netzsch Gerätebau. Expansions of the samples during the measurements were neglected. For the laser-flash apparatus, we cut out discs from the CLHSM at different positions and with different orientations before and after thermal cycling (Figure 2). The discs had thickness of 3 or 5 mm and a diameter of 12.7 or 25.4 mm. For less homogenous samples, larger discs were used.

We measured the discs up to 210°C, which is 10°C below the melting point of K-NaNO3-eu. At this temperature, no melting of the disc surface due to the laser beam was observed. Thermal diffusivity measurements resulted in reduced values for measurements carried out in the cooling segment compared to the heating segment. Subsequent measurements in the heating segment followed approximately the values measured in the previous cooling segment. Determination of the mass and dimensions of the sample before and after the measurement resulted in only small deviations. These deviations could not explain this hysteresis effect. We concluded that some structural change of the CLHSM during the first heating segment occurred. Hence, the thermal diffusivity values were generally obtained from the cooling segment. For all measurements, the Cape-Lehmann model with pulse correction adapted by the Netzsch software was used. The laser power was selected as small as possible such that a suitable signal-to-noise ratio for the analysis was obtained. Typically, the correlation coefficient between model and measurement was higher 99%. For each temperature, thermal diffusivity values from at least three measurements were averaged. Some compressed samples showed a poorer match between model and measurement. This was probably caused by large salt inclusions in the disc compared to the discs size. In this case, the correlation coefficient was always higher 95%.

Figure 2: Position and Orientation of the Laser-Flash Discs in the CLHSM
4. DISCUSSION OF EXPERIMENTAL RESULTS

4.1 Impact of Thermal Cycling

For all samples, thermal cycling did not result in a significant mass loss. Generally, there was a trend of sample expansion (or lower density). This trend was most pronounced for the compression and infiltration route using CEG (Table 1). For the CEG sample, considerable segregation due to the thermal cycling was observed. Thermal cycling tests in an evaporating dish showed that the form stability of the CEG composite is generally high, although some leakage of salt was observed. This result also demonstrates that not all salt remains in the CEG matrix during cycling. Hence, we cut out laser-flash discs from positions in the CLHSM where the graphite matrix remained intact. The NG composite showed the best performance compared to the two other composites in terms of segregation, form stability and expansion.

4.2 Thermal Conductivity Results for the Compression Route

Figure 3 presents thermal conductivity results of the compression route. They were obtained by thermal diffusivity measurements with the laser-flash apparatus and the additional assumptions described in the experimental procedure section. The samples varied in the graphite fraction (10, 20 and 30% by weight) as well as the specimen position and orientation in the CLHSM (Figure 2). All but one measurement were carried out using samples without thermal cycling. For comparison, literature values of the salts KNO3, NaNO3 and K-NaNO3 are also shown [Janz 1979]. The graphite fraction of the composite decisively impacts on the effective thermal conductivity of the composites (Figure 3). Values vary an order of a magnitude from about 3 W/mK (10% graphite by weight) up to about 30 W/mK (30% graphite). Measurements also showed a slight tendency of reduced thermal conductivities for higher temperatures. For the 30% sample for Orientation 2, the thermal conductivity values differed by about a factor two. The position in the CLHSM was the only difference between these two samples. This result also confirms the spatial heterogeneity already observed while determining the composition of the compressed samples. The influence of thermal cycling seems to be rather weak, although there is some uncertainty about this statement due to the different positions in the CLHSM and the single measurement. For this reason, a more detailed examination of this aspect is required. The impact of the sample orientation cannot be clearly answered, since thermal conductivity differences may also stem from differences due to the sample position (heterogeneity of the CLHSM). For the 20 and 30% samples in orientation 1, the thermal conductivity measurements could be closely reproduced. This reproducibility is believed to be the result of a close position of the laser-flash discs cut out from the CLHSM.

![Figure 3: Thermal Conductivity of the CLHSM using the Compression Route before and after Thermal Cycling.](image-url)
4.3 Thermal conductivity results for the infiltration route – NG

As for the compression route, thermal conductivity values spread widely depending on the position in the CLHSM (Pos 1 to 3, Figure 4). This variation is also believed to be caused by the heterogeneity of the CLHSM. No major reduction due to thermal cycling could be identified. A detailed assessment of this aspect would require a thermal conductivity measurement, thermal cycling and a repetitive conductivity measurement of the same sample.

Figure 4: Thermal Conductivity of the CLHSM using the Infiltration Route for NG Flakes before and after Thermal Cycling (Graphite Content 30% by Weight).

4.4 Thermal conductivity results for the infiltration route - CEG

The thermal conductivity of the CLHSM prepared by the CEG infiltration route can be expected to be dominated by the porous graphite matrix [Py 2001]. Compression of EG induces some orientation in the material, in such a way that every graphite sheet tends to lie within a plane perpendicular to the pressing stress. Additionally, since each individual graphite flake exhibits anisotropic properties due to its layered structure, anisotropy is thus expected in the CEG plates. Celzard summarized measurement results of CEG plates with different densities, where thermal conductivities in the plane perpendicular to the pressing stress were generally higher than thermal conductivities in plane with the direction of pressing [Celzard 2005].

Findings reported by Celzard translate in lower thermal conductivities in through-plane compared to the in-plane direction in this work. Hence, the reported through-plane thermal conductivity results can be considered as a lower bound (Figure 5). The thermal conductivity values of the CLHSM are approximately in agreement with values reported for a single CEG plate with a density of 0.07 g/cm³ [Celzard 2005]. Considering the low graphite content of the CEG route, thermal conductivity values can be regarded as high compared to the other routes. Although the conductivity values are slightly below the target of 5 W/mK. As for the previous routes, also the CEG route showed some conductivity variations depending on the position in the CLHSM (Figure 5). Cycled specimens did not show a pronounced spread of conductivity values (Figure 5). This may be the result of a closer position of the laser-flash disc in the cycled CLHSM or an improved CLHSM homogeneity due to the cycling. In particular the cycled samples showed some weak reduction of the thermal conductivity with increasing temperature.
5. CONCLUSION AND OUTLOOK

For the application in high temperature latent heat storage systems, new composite materials based on an alkali nitrate mixture and different graphite types were prepared. As a PCM the eutectic KNO₃-NaNO₃ with a melting temperature of 220°C was used. We examined different preparation routes using natural graphite flakes, ground expanded graphite particles and compressed expanded graphite plates to enhance heat transfer of the poorly conducting PCM.

This work showed that the laser-flash technique is a suitable method to characterize composite latent heat storage materials (CLHSM). Laser-flash measurements above room temperature resulted in a trend of decreasing thermal conductivity with increasing temperature. This trend is in agreement with a previous study using the comparative method [do Couto Aktay 2005].

Both laser-flash measurements and composition determinations of the specimens showed that the CLHSM exhibit a considerable heterogeneity. Composites of all preparation routes showed an enhancement of the thermal conductivity in the range from 3 to 30 times, if compared to the single PCM. Values were close or within the target range from 5 to 15 W/mK. However, absolute thermal conductivity values are not the only criteria to select the most promising preparation route. Generally a small graphite fraction of the composite is desirable in order to achieve high storage densities and keep costs low. Taking this aspect into account, the infiltration route using the CEG plate is currently regarded as the most suitable route. Results of this work confirm that composites prepared by the CEG route reach high effective thermal conductivities with a small graphite fraction. The effective thermal conductivity is dominated by the conductivity of the interconnected graphite structure.

Future work will focus on the improvement of the thermal cycling behavior (salt leakage) of the CLHSM and the adaptation of the characterization procedure in order to exclude the heterogeneity effects of the composites. The latter should allow a detailed assessment and understanding how thermal conductivity values depend on thermal cycling and the direction of measurement.
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