PCM-Graphite Composites for High Temperature Thermal Energy Storage

Thomas Bauer
DLR – German Aerospace Center
Institute of Technical Thermodynamics – Stuttgart
Co-Authors: Rainer Tamme, DLR; Martin Christ, Oswin Öttinger, SGL Technologies GmbH

The Tenth International Conference on Thermal Energy Storage,
Contents

Presentation is directed to fundamental aspects and correlation between material properties and manufacturing routes of PCM-graphite composites

Part of the work is funded by the Federal Ministry of Education and Research (BMBF) under contract 03SF0307A-F (LWSNet)

- Introduction
- Characterization of alkali nitrate salts
- Preparation and characterization of PCM-graphite composites
- Conclusions
Applications for PCM-Graphite Composites

High temperature applications
- Improved energy efficiency (Industrial process heat, CHP)
- Renewable energy (e.g. Solar thermal power)

Low temperature applications (e.g. Comfort Heating)
Materials for High Temperature Thermal Storage

- **Sensible heat storage materials**

- **Phase change materials (PCM)**
  - Single or 2-phase heat transfer fluid
  - Virtually isothermal operation
  - Heat transfer limitations
    - Increased surface area
  - **Composites**
    - Alkali nitrate salts as PCM
    - Graphite to enhance heat transfer
Selected Alkali Nitrate/Nitrites as PCMs

Enthalpy [J/g] vs Temperature [°C]

- LiNO$_3$
- LiNO$_3$-NaNO$_3$
- KNO$_3$-LiNO$_3$
- NaNO$_2$
- NaNO$_3$
- KNO$_3$-NaNO$_2$-NaNO$_3$
- KNO$_3$-NaNO$_3$
- KNO$_3$
KNO₃-NaNO₃ – Phase Diagram

Eutectic composition:
- Melting temperature 220°C
- Enthalpy 100 J/g

Eutectic KNO3-NaNO3 – Heat Capacity $c_p$
Differential Scanning Calorimeter (DSC)

Heat capacity [J/(g.K)]

Temperature [°C]

- Voskresenskaya
- Voskresenskaya liquid
- Kamimoto
- Carling
- Tufeu
- Janz 1982
- Nguyen-Duy
- DLR

Error bar 10%
NaNO3 – Thermal Diffusivity $\alpha$
Laserflash

Temperature [°C]

Thermal diffusivity [mm$^2$/s]

- Gustafsson
- Tufeu (exp.)
- Tufeu (comp.)
- Kobayasi
- Odawara
- Ohta
- Zhang
- Kato
- DLR 1
- DLR 2
- DLR 3

Error bar 5%
Alkali Nitrate Salts – Thermal Conductivity

\[ k = \alpha \cdot \rho \cdot c_p \]

![Graph showing thermal conductivity of alkali nitrate salts vs. temperature]
Pipe number can be reduced significantly for PCM conductivities from 5 to 15 W/mK
Types of Graphite and Composite Preparation Route

1. Vacuum/pressure infiltration process using **Natural graphite**
2. Infiltration process using **Compressed expanded graphite plates**
3. Compression using **Ground expanded graphite**
Characterization of the Composites, Position and Orientation of the Laserflash Discs

Sample for thermal conductivity - in-plane

Sample for thermal conductivity - through-plane direction after thermal cycling
Natural Graphite Composite
Thermal conductivity

30wt% graphite

Through-plane, Pos. 1
Through-plane, Pos. 2
Through-plane, Pos. 3
Through-plane, Pos. A, cycled
Through-plane, Pos. B, cycled
K-NaNO3(eu)
NaNO3
KNO3

Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

Folie 13 > PCM-Graphite Composites for High Temperature Thermal Energy Storage > Thomas Bauer
Natural Graphite Composite
SEM Pictures

30wt% graphite

<table>
<thead>
<tr>
<th>Before thermal cycling</th>
<th>After 10 thermal cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Before thermal cycling" /></td>
<td><img src="image2.png" alt="After 10 thermal cycles" /></td>
</tr>
</tbody>
</table>

- Graphite
- KNO$_3$-NaNO$_3$
Compressed Composite
Thermal conductivity

- 30%, Orientation 1, Pos. 1
- 30%, Orientation 1, Pos. 2
- 30%, Orientation 2, Pos. 1
- 30%, Orientation 2, Pos. 2
- 20%, Orient. 1, Pos. with little salt
- 20%, Orient. 1, Pos. with plenty salt
- 20%, Orientation 1, Pos. 1
- 20%, Orientation 1, Pos. 2
- 20%, Orientation 1, Pos. A, cycled
- 20%, Orientation 1, Pos. B, cycled
- 10%, Orientation 1
- 10%, Orientation 1, cycled

- K-NaNO3(eu)
- NaNO3
- KNO3

Temperature [°C]

Folie 15 > PCM-Graphite Composites for High Temperature Thermal Energy Storage > Thomas Bauer
Compressed Composite SEM Pictures

<table>
<thead>
<tr>
<th>Before thermal cycling</th>
<th>After 10 thermal cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td></td>
</tr>
<tr>
<td>NaNO₃ prilled</td>
<td></td>
</tr>
<tr>
<td>GFG500</td>
<td></td>
</tr>
</tbody>
</table>
Composite made of the infiltrated Matrix

Thermal conductivity

5wt% graphite, density of the matrix 0.07 g/cm³

Source: SGL CARBON GROUP

Folie 17 > PCM-Graphite Composites for High Temperature Thermal Energy Storage > Thomas Bauer
Composite made of the infiltrated Matrix

SEM Pictures

5wt% graphite, density of the matrix 0.07 g/cm³

<table>
<thead>
<tr>
<th>Before thermal cycling</th>
<th>After 10 thermal cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="SEM Picture" /></td>
<td><img src="image2" alt="SEM Picture" /></td>
</tr>
</tbody>
</table>

Porosity
Conclusions

- PCM storage attractive for 2-phase heat transfer fluid systems
- Single salt properties mostly in agreement with literature values
- With PCM-Graphite composites suitable effective thermal conductivities can be achieved
- SEM and Laserflash examinations indicate thermally stable graphite structure in the composite
- Of the investigated manufacturing routes, the infiltration route has the potential for high effective conductivities with a low graphite fraction
- Infiltration route needs still further R&D to realize composite materials with sufficient PCM content

Thank You for Your Attention