Metallic Composites Phase-Change Materials for High-Temperature Thermal Energy Storage

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Rutgers University

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Thermal Scientist

Sohae Kim
Heat Transfer Scientist

Hengzhi Wang
Materials Scientist

Hui Wang
Materials Scientist
Background – Thermal Storage

Concentrated Solar Power

Affected by weather and night-time

Proposed Solution:
High temperature, high latent heat
thermal storage materials

Nuclear Power Plant

Lack peaking power capacity

Source: http://www.aaenvironment.com/GreenNuclear.htm
Project Goals

- High temperature eutectic PCM \( (550-900^\circ c) \)
- High latent heat PCM \( (> 400kJ/kg) \)
- High thermal conductivity \( (> 10W/mK) \)

Strategies

- Nanoparticle/ternary increase latent heat \( (50\%) \)
- Earth abundant materials
- Low cost materials
Direction for Increasing Latent Heat

High latent heat metallic composites with high thermal conductivity

Two Phase Separated in Solid

Latent Heat (Enthalpy of Fusion $H$)

Two Phase Mixed in Liquid

$\Delta H = T \Delta S$

More Configuration

-> Configurational Entropy $S$
Eutectic composition: phase separation for maximum mixing entropy

Eutectic Alloys as PCM

Typical Binary Phase Diagram with Eutectic Composition

Microstructure of Al-12Si eutectic alloy

M.M. Makhlof, H.V. Guthy, J. Light Metals 1, 2001
Understanding of Latent Heat

\[
\Delta S = \Delta S_{\text{mixing}} + \Delta S_{c_p} + (1 - x_e) \frac{\Delta h_{f,A}}{T_{m,A}} + x_e \frac{\Delta h_{f,B}}{T_{m,B}}
\]

Mixing entropy  Sensible heat  Latent heat from each elements
Latent Heat from Mixing Entropy

Ideal Mixing:

$$\Delta s_{\text{mixing}} = -R \sum x_i \ln x_i$$

At 800K, with atomic mass of 30 g/mol, latent heat from mixing:
- Binary alloy: 156 kJ/kg
- Ternary alloy: 245 kJ/kg
Material Selection – Latent Heat

\[ \frac{\Delta H}{T_m} (\text{kJ/kg.K}) \]
Material Selection – Vapor Pressure, Price

<table>
<thead>
<tr>
<th>Instable Elements</th>
<th>Stable Elements for Melting</th>
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</thead>
<tbody>
<tr>
<td>Vapor Pressure</td>
<td>= 100 kPa</td>
</tr>
<tr>
<td>Li @ 722 C</td>
<td>B @ 2075 C</td>
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<tr>
<td>Na @ 880 C</td>
<td>Fe @ 1455 C</td>
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<tr>
<td>Mg @ 1088 C</td>
<td>Al @ 1209 C</td>
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<tr>
<td>P @ 276 C</td>
<td>Co @ 1517 C</td>
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<tr>
<td>S @ 444 C</td>
<td>Si @ 1635 C</td>
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<tr>
<td>K @ 756 C</td>
<td>Ni @ 1510 C</td>
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<tr>
<td>Ca @ 1482 C</td>
<td>Ti @ 1709 C</td>
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<td>Zn @ 912 C</td>
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<tr>
<td>Pb @ 1754 C</td>
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<tr>
<td>Sb @ 1585 C</td>
<td>Cr @ 1383 C</td>
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<td>Mo @ 2469 C</td>
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<td>Mn @ 955 C</td>
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<td>Sn @ 1224 C</td>
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<td>C - with 10 Pa @ 2566 C</td>
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</table>

Vapor Pressure = 1 Pa

Price ($/lb)

- Ti
- Bi
- Sn
- Ni
- Sb
- Cu
- Mg
- Al
- Si, Zn, Pb
- Fe
# Invariant Temperature of Binary Alloys

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<tr>
<th>B</th>
<th>C</th>
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<th>Si</th>
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**Invariant means the melting temperature does not change during phase change**

**Red:** eutectic

**Green:** compound

**Black:** element

**---:** no invariant temperature

**NA:** phase diagram not identified
Latent Heat of Fusion ~ Melting T

Data based on literature (not verified)
Materials Fabrication Facilities
Materials Characterization Facilities
Al-12Si (at%) Eutectic Alloy

Hot-Press: Pressure: 80 Mpa, Temperature: 577 °C

Diameter: 12.7 mm
Thickness: 1.5-2.8 mm
### Latent Heat of Al-12Si Alloy

<table>
<thead>
<tr>
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<th>Melting $T$ (°C)</th>
<th>Latent Heat (kJ/kg)</th>
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<tbody>
<tr>
<td><strong>Measured value</strong></td>
<td><strong>578.3</strong></td>
<td><strong>554.9</strong></td>
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<tr>
<td>Reference value</td>
<td>576</td>
<td>560</td>
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</table>

![DSC Graph](image)

- Onset: 578.3°C
- Area: 554.9 J/g
Estimation of Al-12.2Si (at%)

Estimated Latent Heat: 511kJ/kg

- Melting of Al: 318kJ/kg
- Melting of Si: 114kJ/kg
- Ideal mixing: 79kJ/kg
- Discrepancy from Exp.: 44kJ/kg

Possible causes:
- Sensible Heat?
- Non-ideal Mixing?
Thermal Conductivity of Al-12Si Alloy

Thermal Conductivity: 122 W/mK  (500 °C, Cp from literature)

Thermal diffusivity of eutectic Al-12Si alloy (LFA 457 MicroFlash, Netzsch)
Hypereutectic Al-28Si Alloys

- **Temperature range:** 576.8 to 815 °C
- **Latent heat:** 753.2 kJ/kg
- 448 kJ from eutectic alloy
- 305 kJ from additional Si and sensible heat

Graph showing:
- **Area:** 448.1 J/g (main peak only)
- **Area:** 753.2 J/g (whole area)
Ternary Phase Diagram
Ternary Alloy # 1

Ternary alloy A-B-C

Latent heat: 867 kJ/kg
Estimated: 964 kJ/kg

Contribution from:
Mixing entropy: 304 kJ/kg
Material A: 187 kJ/kg
Material B: 433 kJ/kg
Material C: 41 kJ/kg

1/3 from mixing entropy!
Summary

• Systematically investigated metallic PCMs from unary to ternary alloys.
• Binary 87.8Al-12.2Si (at%) alloy: 554.9 kJ/kg at 578.3 °C
• Ternary alloy #1: 865 kJ/kg around 850 °C
• Thermal conductivity > 100 W/m.K
Future Directions

• Further improving materials
  • Quaternary alloys and eutectics
  • Compounds + eutectics
  • Additives

• Packaging of materials

• Systems and applications