High-Temperature Coating for Solar-Thermal Energy Conversion

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Sponsors:
Concentrating Solar Power (CSP)
Concentrating Solar Power (CSP)

DOE Report: “2014: The year of CSP”
CSP: Cumulative Installed Capacity

Source: “Technology Roadmap: Solar Thermal Electricity”, IEA
CSP: Thermal Energy Storage

Use of storage for shifting production to cover evening peaks

Notes: the graph shows on left scale the DNIR and the flows of thermal exchanges between solar field, storage and power block, and on the right scale electricity generation of a 250-MW (net) CSP plant with storage. Courtesy of ACS Cobra.

Source: “Technology Roadmap: Solar Thermal Electricity”, IEA
DOE Sunshot Initiatives on CSP

Target LCOE in Y2020: 6¢/kWh (cf. 21¢/kWh in Y2010, 13¢/kWh in Y2013)
There is an optimal working temperature for any given concentration ratio.

Source: “Technology Roadmap: Solar Thermal Electricity”, IEA
Next-Generation CSP Systems

CSP Subsystem Interface Coupling
A: Solar Field and Receiver
B: Receiver and Heat Transfer Fluid System
C: Receiver and Energy Storage
D: Power Block to Receiver
E: Power Block to Energy Storage

Solar receiver requirements to achieve the target LCOE:
-- HTF exit temperature ~720°C, Thermal eff. ≥ 90%, Lifetime ≥ 10k cycles

DOE Sunshot FOA “APOLLO”
Solar Selective Coating

Figure of Merit (FOM) is determined by absorptance in the solar spectrum and IR emittance

\[ FOM = \frac{\int_0^\infty (1 - R(\lambda))I(\lambda)d\lambda - \frac{1}{C} \left[ \int_0^\infty (1 - R(\lambda))B(\lambda, T)d\lambda \right]}{\int_0^\infty I(\lambda)d\lambda} \]

- FOM depends on solar concentration ratio \( C \) and absorber surface temperature \( T \)
- Assuming \( C=1000 \) and \( T=750^\circ C \) for Solar Towers
- For high \( C (>1000) \), the infrared emission loss is relatively less important.

## Requirements for Next-Gen Solar Receivers

1. **High Figure of Merit (Thermal Efficiency):**
   
   >= 0.90 (90% efficiency)

2. **High Temperature Stability and Reliability:**
   - at 750 °C under air environment
     - Oxidation resistance
     - Crystal structure stability without decomposition
     - No delamination of SSC layer from metal tube substrate

3. **Low-cost Fabrication**

- DOE SunShot Project’s Milestone (Y2012-2015)
Spinel Oxides as SSC Materials

Why spinel oxides?

- Suitable optical properties (also adjustable with atomic composition)
- Cheap, abundant
- Already oxidized (more stable at high T)
- Scalable synthesis (e.g. hydrothermal and sol-gel synthesis)

Cu$_{1.285}$Fe$_{0.43}$Mn$_{1.285}$O$_4$ Film on Al Substrate[1]

Copper Chromite [2]

a: without SiO$_2$ binder; b, c: with SiO$_2$ binder

Hydrothermal Synthesis: Cu-Contained Spinel NanoParticles

Copper Chromites

- **CuCl₂ 2H₂O 1M Solution**(aq)
- **CrCl₃ 6H₂O 1M Solution**(aq)

Mixing for 5h at RT

Co-Precipitation with 10M NaOH Solution**(aq)

Cu-Cr Hydroxide

Mixing for 2h at RT

Hydrothermal Synthesis at 200°C / 20h

Cu-Fe-Mn Oxides

- **CuCl₂ 2H₂O 1M Solution**(aq)
- **FeCl₃ 6H₂O 1M Solution**(aq)
- **MnCl₂ 4H₂O 1M Solution**(aq)

Mixing for 5h at RT

Co-Precipitation with 10M NaOH Solution**(aq)

Cu-Fe-Mn Hydroxide

Mixing for 2h at RT

Hydrothermal Synthesis at 200°C / 20h

Post-Treatment

- Centrifuging & Washing
- Freeze-Drying
- Crystallization at 550°C/5h/Air
- Spinel Metal Oxide NPs
Scalable Coating Process

1. Prepared diluted resin using ultrasonic Probe stirring
2. Added Black Oxide Powders to the resin
3. Ball milling together for 24hrs
4. Spray-coated Black Oxide slurry on the surface of sand-blasted Inconel alloy coupons (HTF metallic tube material)
5. Cured coated layer material at high temperature
Copper Chromites NPs Synthesized with Different Conditions

- Copper chromites synthesized with 2 different atomic compositions.
- Crystallization condition as a final step of synthesis to be optimized.

<table>
<thead>
<tr>
<th>Atomic Comp.</th>
<th>Crystallization: 550°C/5h/Air</th>
<th>Crystallization: 750°C/2h/Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Cr=1/1</td>
<td>(a) APS&lt; 50 nm</td>
<td>(b) 200-600 nm</td>
</tr>
<tr>
<td></td>
<td>(c) APS&lt; 50 nm</td>
<td>(d) 0.3-1µm</td>
</tr>
<tr>
<td>Cu/Cr=1/2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
XRD and Thermal Stability of CuCr$_2$O$_4$ NPs

- CuCr$_2$O$_4$ can be confirmed.

- Thermally stable at 750°C:
  a. After thermal test, new phase was not seen.
  b. Particle size grown by sintering effect at high temperature.

- Crystal information:
  Tetragonal System
  Lattice: Body-centered
  Cell Parameters: a 6.030, c 7.782
  Main plane: (211) at $2\theta=35.19^\circ$

Crystallization Condition Optimization for CuFeMnO$_4$ NPs

- Cu-Fe-Mn Oxide NPs synthesized with Cu/Fe/Mn=1/1/1 (a/a).
- Optimized crystallization condition: 550 °C / 5h /air, to obtain smaller NPs.

(a) Crystallized at 550°C/5h/air  (b) Crystallized at 750°C/2h/air
XRD and Thermal Stability of CuFeMnO$_4$ NPs

- CuFeMnO$_4$ can be confirmed.

- Thermally stable at 750$^\circ$C:
  a. After thermal test, new phase was not seen.
  b. Particle size grown by sintering effect at high temperature.

* PDF 00-020-0358.
First we tried mixing both compounds.

Max FOM = 0.894

Then we layered both compounds.

Max FOM = 0.902
UCSD’s Black Oxide Coating

-- Typical absorptivity of 97 – 98% in the visible to NIR regime. [For power tower type applications with concentration factor of ~1,000, the absorptivity dominates the solar to heat Figure-of-Merit (FOM), with the blackbody emissivity effect being negligible.]

-- CFM/CuCr: highest FOM (0.902)
-- Pyromark 2500 : FOM of 0.889
High-Temperature Spectrally Selective Coating

\[
FOM = \frac{\int_0^\infty (1 - R(\lambda))I(\lambda)d\lambda - \frac{1}{C} \int_0^\infty (1 - R(\lambda))B(\lambda, T)d\lambda}{\int_0^\infty I(\lambda)d\lambda}
\]

For low \( C \) (e.g., \( \sim 100 \) for troughs), the infrared emission loss is important

\[\Rightarrow \text{Need to improve the selectivity}\]

Trough Collectors

Solar-Thermoelectrics

DOE Report: “2014: The year of CSP”

Black Oxide + TCO for High Selectivity

- We use Al-doped ZnO (AZO) as the TCO
  - Low cost (compared to ITO)
  - Adjustable cutoff wavelength
  - Scalable synthesis
**Atomic Layer Deposition (ALD) of AZO**

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>$\mu$ (cm$^2$/Vs) (at n=\textasciitilde1x10^{21}$cm^{-3}$)</th>
<th>$\varepsilon''$</th>
<th>Scalability</th>
<th>Conformality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed Laser Deposition$^{[1]}$</td>
<td>47</td>
<td>0.5</td>
<td>Poor</td>
<td>Fair</td>
</tr>
<tr>
<td>Sputter$^{[2]}$</td>
<td>8</td>
<td>-</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Atomic Layer Deposition$^{[3]}$</td>
<td>9.8</td>
<td>0.47</td>
<td>Good</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

- Self-limiting surface reactions
- “Monolayers” are deposited by diethly zinc, water and trimethylaluminum pulses
- Chemical composition controlled by the ratio of chemical pulses
- Thickness controlled on the angstrom scale
- Extremely high conformality

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$^{[2]}$Jia et.al Thin Solid Films 559 (2014) 69–77

$^{[3]}$Riley et. al. Small, *accepted*
Selective Transmission of AZO

Graph showing transmission as a function of wavelength for:
- AZO (1um) After Annealing
- AZO (1um)
- Glass
Summary and Future Directions

• We have developed solar absorbing coating based on nanostructured black oxides
  – Thermal efficiency (FOM) > 90%
  – Stable at high temperature
  – Scalable synthesis and coating process
  – Suitable for next-generation solar towers.

• On-field evaluation of the black oxide coating
• Black oxide + TCO for high-temperature selective coating
• Integration into high-temperature solar-thermal systems