DEVELOPMENT OF SOLAR SELECTIVE CERMETS BY DC MAGNETRON SPUTTERING: INTRUMENTAL ADVANCES AND OPTICAL PROPERTIES

R. Escobar Galindo, E. Céspedes, J. A. Sánchez, J. M. Albella, C. Prieto
Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)

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MOTIVATION

ICMM-CSIC: Development of new coating materials for thermal collectors.
Increasing the energy absorbed by receiver reduces the costs.

Development of new more efficient selective coatings thermally stable above 500ºC with both high solar absorptance (>0.96) and low thermal emittance (<0.06)
An ideal selective coating should present an **abrupt transition of reflectance** spectrum between the visible and IR range.

- The energy of this transition (**cut-off**) depends on the operating temperature (shift of the blackbody emission)
Cermet materials: nanometer-sized particles (∼1-20 nm) embedded in a ceramic matrix.
Metallic substrate, antireflection coating to enhance the solar absorptance.
Grading from low metal (LMVF) to high metal (HMVF) particle density in depth improves the spectral selectivity of the coatings.
Best optical results for two-cermet layers with different metal concentration
Commercially available double cermet Mo-SiO₂ based absorbers
TECHNICAL APPROACH

Optical modelling to design and extract optical constants

Coating characterisation material and optical properties

PVD deposition of high-temperature solar-selective coatings

HITECO
Higher reflectance with higher metal volume fraction.

- Selectivity of cermets based on a **tandem effect**: strong absorption in the visible region (below 1 µm) and is almost transparent in the IR range.
Oscillations related to the interference between cermet and substrate

Minimum reflectance shift towards high wavelengths with thickness
OPTICAL MODELLING: SELECTIVE COATINGS

Select-1

- \( \alpha = 0.93 \) (0.25→2.5 \( \mu m \))
- \( \alpha = 0.93 \) (0.3→1.7 \( \mu m \))
- \( \varepsilon_{82^\circ C} = 0.07 \) (1→30 \( \mu m \))

Select-2

- \( \alpha = 0.91 \) (0.25→2.5 \( \mu m \))
- \( \alpha = 0.92 \) (0.3→1.7 \( \mu m \))
- \( \varepsilon_{82^\circ C} = 0.05 \) (1→30 \( \mu m \))

Select-3

- \( \alpha = 0.92 \) (0.25→2.5 \( \mu m \))
- \( \alpha = 0.94 \) (0.3→1.7 \( \mu m \))
- \( \varepsilon_{82^\circ C} = 0.05 \) (1→30 \( \mu m \))
Higher solar absorptance and lower thermal emittance for selective absorbers based on Si$_3$N$_4$
COATING PREPARATION BY PVD-MAGNETRON SPUTTERING

2 chambers dedicated to the preparation of oxides and nitrides based coatings

- Typically, DC or RF 10-100 W
- Working pressure $10^{-3}$ - $10^{-2}$ mbar
- Layers thickness controlled by the time over each cathode
- Possibility of different working gases during the growth of different layers
COATING PREPARATION BY PVD-MAGNETRON SPUTTERING

E. Céspedes, C. Prieto, R. Escobar, J. Sánchez
Patente OEPM (ES P201131009, June 2011).

Two cermet PVD-strategies:
- Multilayers
- Co-sputtering

Excellent agreement between experimental and optical simulation validates the procedure adopted to fabricate and optimized the solar selective coatings.
COMPOSITION AND STRUCTURAL CHARACTERISATION

GIXRD

Resonant RBS

SEM

EXAFS in progress
OPTIMIZATION OF OPTICAL PROPERTIES

Calculation of “Solar absorbance” \( (\alpha_{\text{sol}}) \)

\[
\alpha_{\text{sol}} = \frac{\int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] A(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} A(\lambda) \, d\lambda}
\]

- \( R \) measurements at RT (UV-VIS-NIR)
- \( A(\lambda) = \) Solar emission ASTM G173-03 Ref. Spectrum (AM1.5) (Wm\(^{-2}\)µm\(^{-1}\))

Calculation of “Thermal Emittance” \( \varepsilon(T) \)

\[
\varepsilon_{\text{th}}(\theta, T) = \frac{\int_{\lambda_1}^{\lambda_2} E(T, \lambda)(1 - R_{\text{th}}(\lambda, \theta)) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E(T, \lambda) \, d\lambda}
\]

- \( R \) measurements at RT (NIR-MIR) \( \Rightarrow \varepsilon_{RT} \)
- Estimation of \( \varepsilon(T) \) using blackbody curves with no variation of \( R(\lambda) \) with \( T \)

\( \alpha = 0.95 \)
\( \varepsilon_{RT} = 0.02 \)
\( \varepsilon_{600^\circ C} = 0.13 \)

Direct measurement of emittance
Emmisometer Model AE1
\( \Delta \lambda = 3 \rightarrow 30 \mu m \)
\( T = 82^\circ C \)
\( \Delta \varepsilon = \pm 0.01 \)

\(- \varepsilon(T) \) in collaboration with J.M. Tello
OPTIMIZATION OF OPTICAL PROPERTIES

<table>
<thead>
<tr>
<th></th>
<th>S2-cosp-SSth</th>
<th>S7-cosp-SS</th>
<th>S14-cosp-SSth (optimized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR: Si$_3$N$_4$</td>
<td>55 nm</td>
<td>40 nm</td>
<td>60 nm</td>
</tr>
<tr>
<td>LMVF</td>
<td>FF = 13%</td>
<td>FF = 22%</td>
<td>FF = 18%</td>
</tr>
<tr>
<td></td>
<td>60 nm</td>
<td>60 nm</td>
<td>55 nm</td>
</tr>
<tr>
<td>HMVF</td>
<td>FF = 18%</td>
<td>FF = 30%</td>
<td>FF = 35%</td>
</tr>
<tr>
<td></td>
<td>60 nm</td>
<td>60 nm</td>
<td>50 nm</td>
</tr>
<tr>
<td>IR mirror</td>
<td>Ag 175 nm</td>
<td>Ag 175 nm</td>
<td>Ti/Ag/Ti/TiN</td>
</tr>
<tr>
<td>Subst.</td>
<td>SSth</td>
<td>SSth</td>
<td>SSth</td>
</tr>
<tr>
<td>Optical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>param.</td>
<td>α = 0.72</td>
<td>α = 0.88</td>
<td>α = 0.95</td>
</tr>
<tr>
<td></td>
<td>ε$_{RT}$ = 0.02</td>
<td>ε$_{RT}$ = 0.06</td>
<td>ε$_{RT}$ = 0.02</td>
</tr>
<tr>
<td></td>
<td>ε$_{600^\circ C}$ = 0.04</td>
<td>ε$_{600^\circ C}$ = 0.19</td>
<td>ε$_{600^\circ C}$ = 0.13</td>
</tr>
</tbody>
</table>

![Graph showing reflectance vs. wavelength for different samples](chart.png)
OPTIMIZATION OF OPTICAL PROPERTIES: THERMAL STABILITY

- air annealing
- vacuum annealing ($p = 10^{-2}$ mbar)

### Table

<table>
<thead>
<tr>
<th>Material</th>
<th>Optical Constants</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>S14-cosp-SSth</td>
<td>$\alpha = 0.95$ (0.3$\rightarrow$1.7 $\mu$m)</td>
<td>$\varepsilon_{450^\circ C} = 0.07$, $\varepsilon_{600^\circ C} = 0.11$</td>
</tr>
<tr>
<td>S14-cosp-SSth-450°C</td>
<td>$\alpha = 0.96$ (0.3$\rightarrow$1.7 $\mu$m)</td>
<td>$\varepsilon_{450^\circ C} = 0.07$, $\varepsilon_{600^\circ C} = 0.10$</td>
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<tr>
<td>S14-cosp-SSth-600°C</td>
<td>$\alpha = 0.95$ (0.3$\rightarrow$1.7 $\mu$m)</td>
<td>$\varepsilon_{450^\circ C} = 0.08$, $\varepsilon_{600^\circ C} = 0.13$</td>
</tr>
<tr>
<td>S14-cosp-SSth-640°C</td>
<td>$\alpha = 0.95$ (0.3$\rightarrow$1.7 $\mu$m)</td>
<td>$\varepsilon_{450^\circ C} = 0.10$, $\varepsilon_{600^\circ C} = 0.15$, $\varepsilon_{640^\circ C} = 0.17$</td>
</tr>
</tbody>
</table>
Metallic IR-mirror alternatives to Ag

<table>
<thead>
<tr>
<th></th>
<th>S10-cos-SS (Cu)</th>
<th>S17-cosp-SSth (Ticusil)</th>
<th>S14-cosp-SSth (Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.72</td>
<td>0.88</td>
<td>0.95</td>
</tr>
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<td>ε_{600°C}</td>
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<td>0.19</td>
<td>0.13</td>
</tr>
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</table>

TUNABILITY:
Cut-off variation by changing the double-CERMET structure (thickness and metal fraction) and deposition (multilayer-cosputtering)
SIMULATIONS USING THE HEAT TRANSFER MODEL

Off-sun simulations:
- ENEA and HITECO S14 able to work at 600°C
- HITECO glass significantly cooler (26°) than the ENEA envelope
FUTURE WORK: AGING MEASUREMENTS AND SCALING UP

• Design of *aging protocol* in collaboration with AIN

\[
P C \alpha_{sol} = -\Delta \alpha_{sol} + 0.25 \Delta \varepsilon_{ther} < 0.05
\]

• **Scaling up** for 0.5 m tubes in progress
FUTURE WORK: MEASUREMENTS AT HIGH TEMPERATURE

- Collaboration with Universidad del Pais Vasco (Prof. J.M. Tello) for in-situ measurements of $\varepsilon(T,\theta)$.

- Collaboration with IMDEA Materiales for in-situ mechanical testing at high temperature (<500°C)

L. del Campo et al.  
CONCLUSIONS

- Optical **simulation** of complete selective coatings stacks from individual layer optical constants \((n,k)\).
- Magnetron sputtering of \(\text{Si}_3\text{N}_4\) based absorber coatings prepared by multilayer and **co-sputtering deposition**.
- Coatings **chemical and optically stable** at 640°C.
- **Cut-off wavelength** tuneable by controlling cermet structure.
- **TiCuSil** as alternative for IR mirror.
- Lab scale coatings fulfil optical requirements ➔ **scaling up** 0.5m tubes.
- In progress: **in-situ** mechanical and optical characterization at high T.
Contact

For further information, please contact us:

Ramon Escobar Galindo: rescobar@icmm.csic.es
Carlos Prieto: carlos.prieto@icmm.csic.es
Eva Céspedes: ecespedes@icmm.csic.es

Website: www.icmm.csic.es