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High-Temperature Solar Selective Coating Development for Power Tower Receivers

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Outline

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III. Approach
IV. Results
V. Future Work

Project Description

- Next-generation power tower temperatures will likely operate at temperatures ≥ 650 °C
- The efficiency of a power tower plant can be increased if the energy absorbed by the receiver is maximized while the heat loss from the receiver to the environment is minimized
- Pyromark® has a high solar absorptance ($\alpha > 0.95$), but also high emittance (ε ~0.87) at the temperatures of interest
- Cermet coatings currently used in troughs have excellent optical properties, but are not well-suited for power tower applications: they are sensitive to oxidation and suffer performance degradation at temperatures > 500 °C

Improved selective absorber coatings for receivers must maintain high absorptance in the solar spectrum but lower emittance in the infrared spectrum. It must also be stable in air, easily applied at large scales, cost effective, and survive thousands of heating and cooling cycles

- At 650 °C, a reduction in ε from 0.88 to 0.4 will increase the thermal efficiency by 4%
- At 800 °C, the same reduction increases the thermal efficiency by 7%
- Levelized cost of energy (LCOE) estimated to be reduced at least 0.25¢/kWh

Project Plans

Optimize, evaluate, and characterize coatings

- Optimize spinel and thermal spray formulations
- Evaluate refractory metal compounds
- Develop surface modification techniques to enhance solar selectivity
- Incorporate cost and durability into LCOE-like metric that can compare coatings across-the-board

Initial on-sun and durability testing

- Performance optimization of coatings supported by isothermal testing at temperature
- Perform tests of candidate selective absorbers applied to tubes and/or plates on sun (furnace and/or tower)
- Evaluate durability of candidates as a function of temperature and heating cycles

Refine coatings and final on-sun testing

- Refine coatings based on optical performance and durability
- Final on-sun tests of most promising selective coatings

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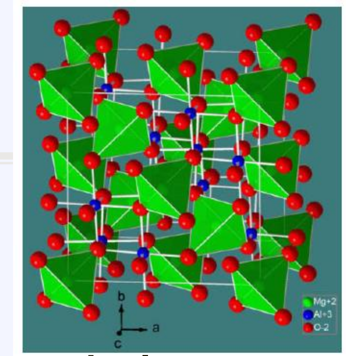
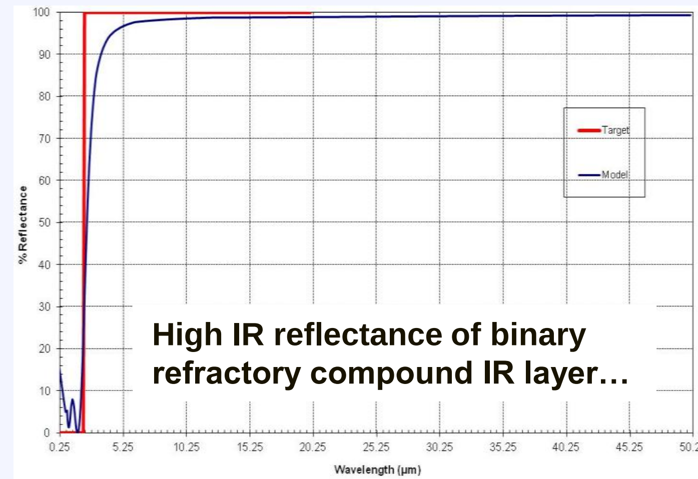
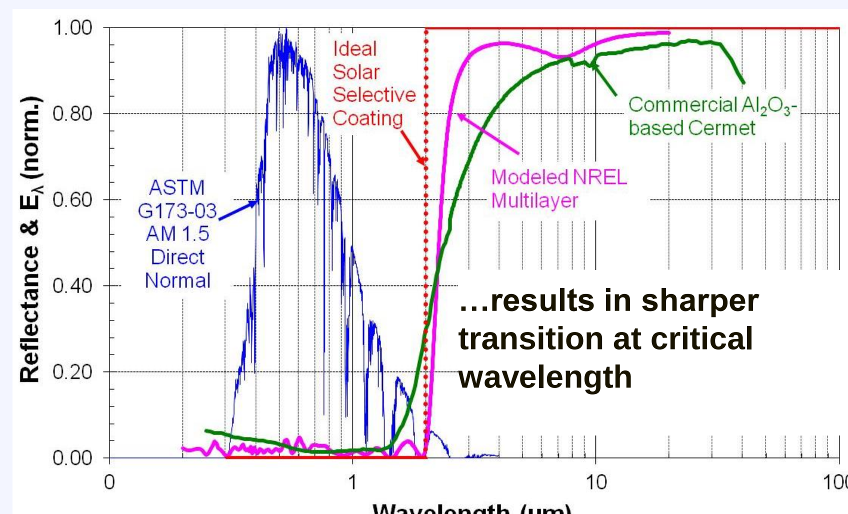
Materials

- Novel materials that are intrinsically solar selective: high α, low ε and stable in air and high temperatures for power towers
- Metal spinel oxides (AB_2O_4):
  - Inherently stable at high temperature and in air
  - Amenable to doping and substitution (e.g. Ni^{2+}, Mn^{2+} and Cu^{2+}), to chemically tailor their properties
- Refractory metal (M) silicides (MSi_2), diborides (MB_2), oxides nitrides and their ternary and quaternary compounds:
  - M = Ha, Ta, Ti, Y, or Zr
  - Intrinsic low UV-Vis-NIR reflectance →high absorptance
  - Intrinsic high IR reflectance →low emittance



Spinel structure





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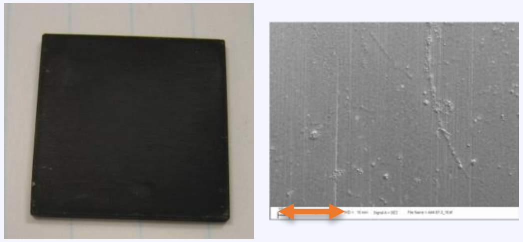
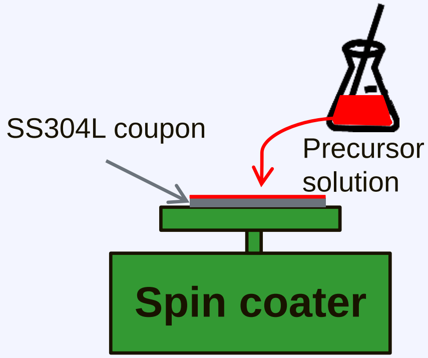
Deposition Methods

- *Spin coating*
  - Facile synthesis of coatings with varying formulations and dopant concentrations
  - Allows for rapid deposition and optical screening of a composition space
- *Electrodeposition*
  - Novel approach to screening solar selective materials
  - Can result in novel surface morphologies

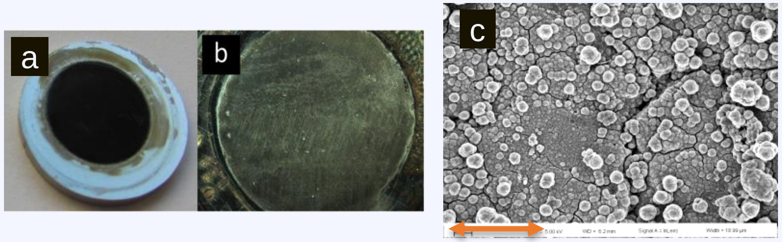


$FeCo_2O_4$ coating (left) and SEM of $FeCo_2O_4$ surface (right). Scale bar = 500 µm.



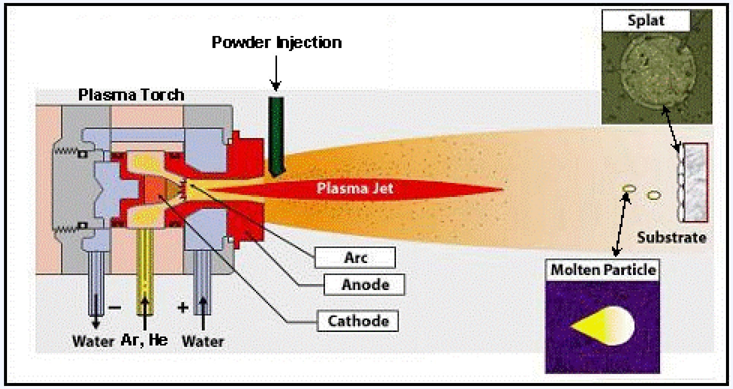
Spin coating (top) and electrodeposition (bottom)

(a) Co_3O_4/SS304L prepared high-T ED method (middle). (b) Image of Co_3O_4 film (deposited for 4h) on SS304L. (c) SEM image is shown at far right (scale bar = 5 um)



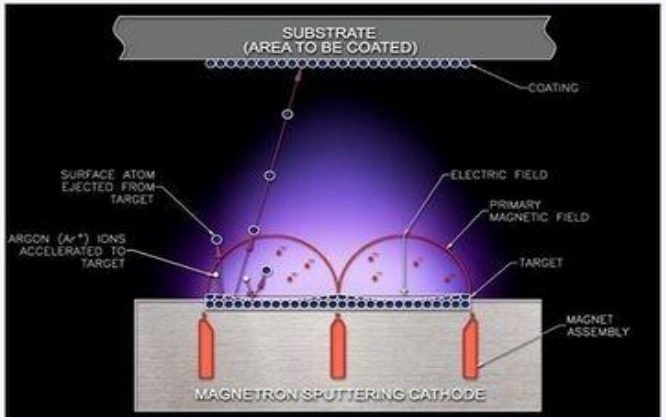
Deposition Methods

- *Thermal Spray*
  - High-surface area coating technique
  - Ability to coat in the field
  - Development of thermal spray techniques to apply pore formers to modify surface morphology in an efficient and cost-effective manner



Air-plasma thermal spraying process for absorber coatings

- *Physical vapor deposition*
  - PVD allows fine control of deposition conditions
  - Deposition conditions control optical, microstructural, & mechanical properties
  - Pulsed DC sputtering is commercial method used for receiver tubes

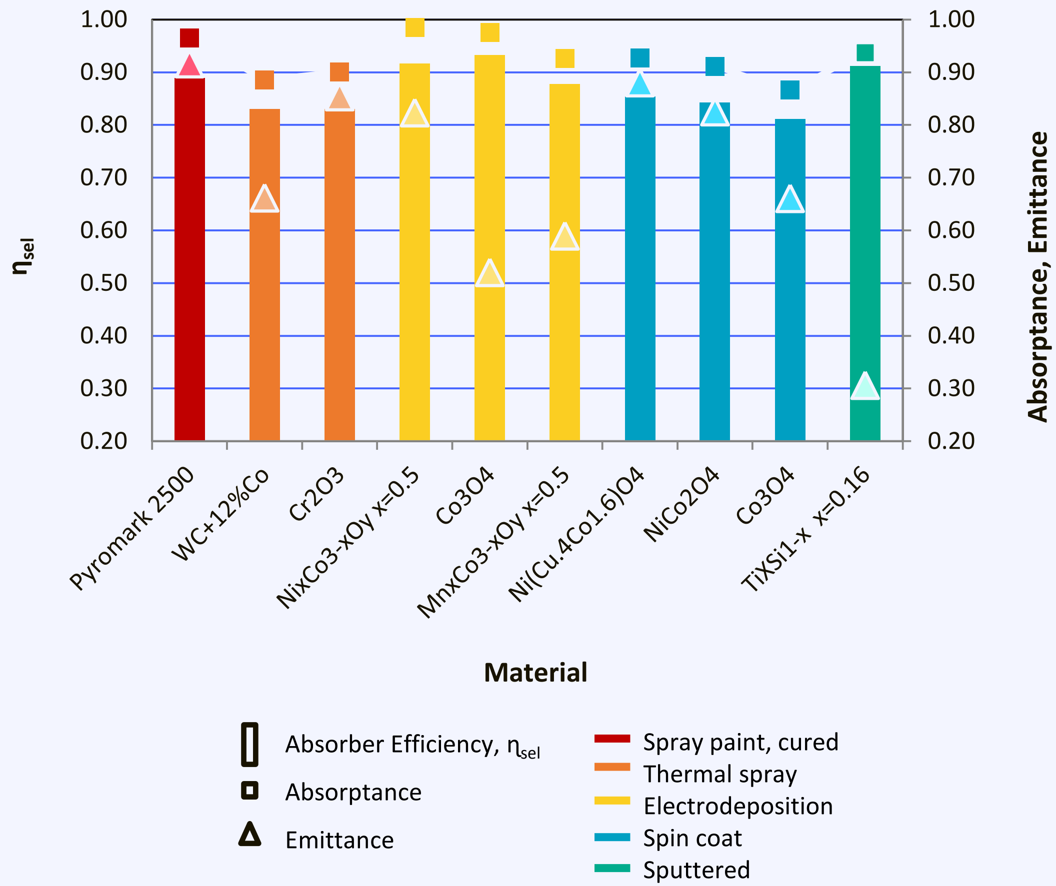


Sputtering (PVD) process for absorber coatings

Figure of Merit, η_{sel}

$$\eta_{sel} = \frac{\alpha_s Q - \varepsilon \sigma T^4}{Q}$$

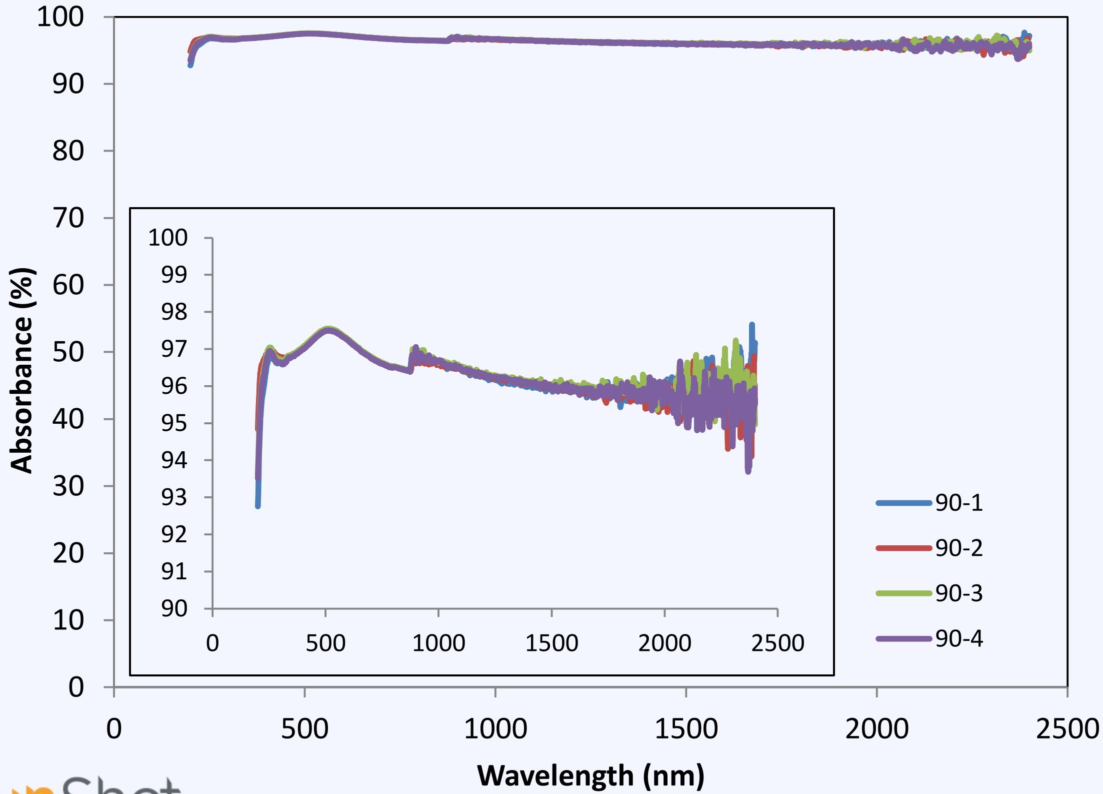
- α_s = solar absorptance
- Q = irradiance on the receiver (W/m^2)
- ε = thermal emittance
- σ = Stefan-Boltzmann constant (5.67x10^{-8} W/m^2/K^4)
- T = surface temperature (K)

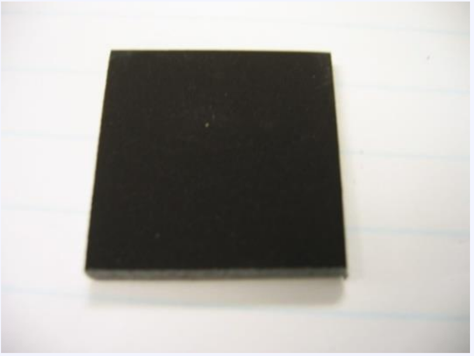


Absorber efficiency, absorptance, and emittance of coatings developed at Sandia and NREL via various deposition techniques. (AOP FY12)

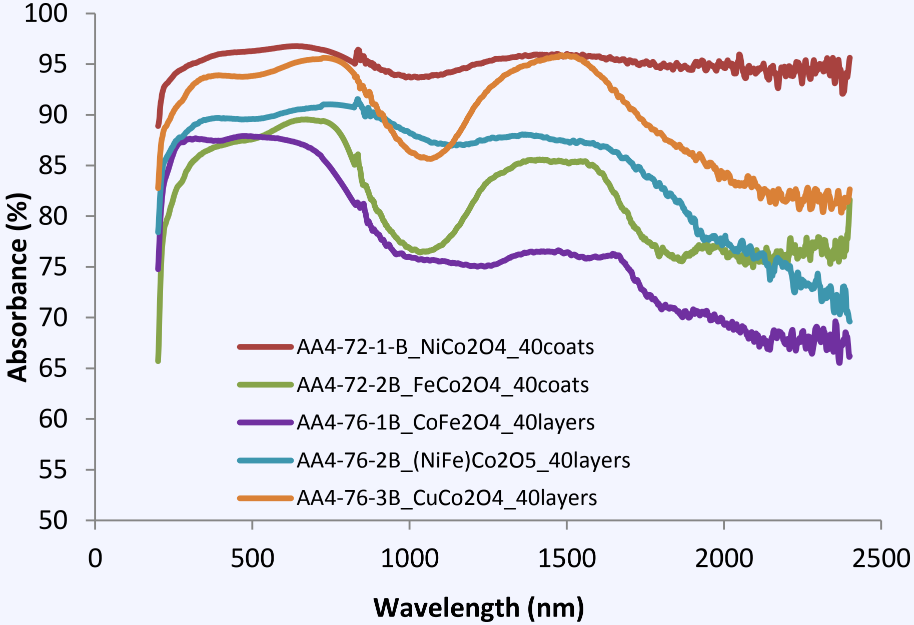
Pyromark 2500

Sample	α (solar)	ε (80C rel)	ε (2400nm)	FOM
Pyromark 2500-1	0.965	0.861	0.972	0.889
Pyromark 2500-2	0.966	0.874	0.950	0.890
Pyromark 2500-3	0.965	0.865	0.950	0.889
Pyromark 2500-4	0.965	0.841	0.956	0.890





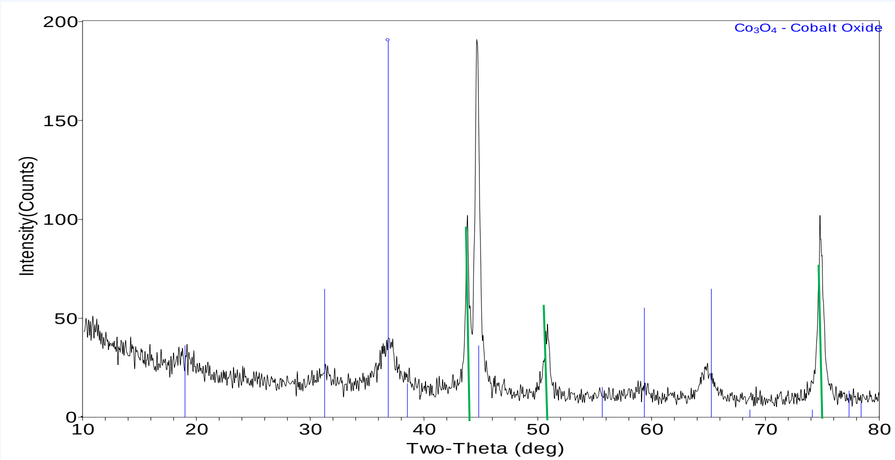
Results-Spin Coated Films



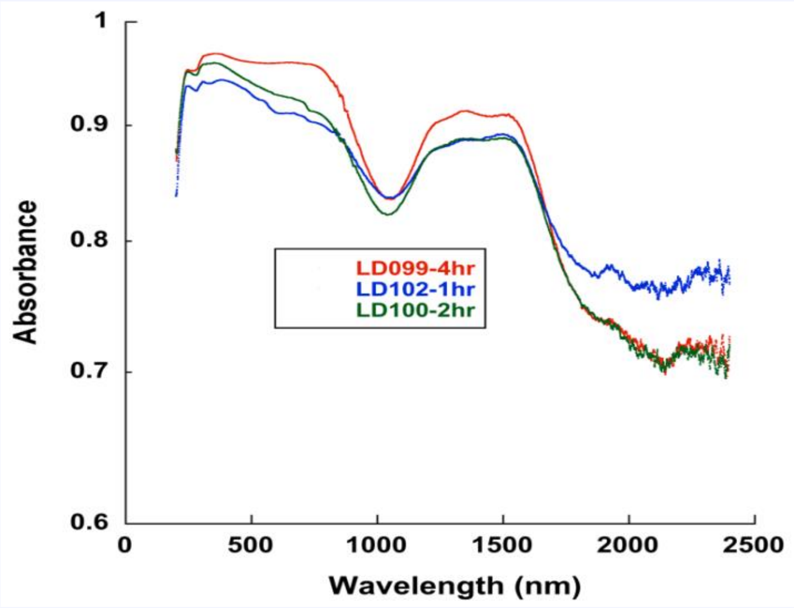
Material	α	ε_{80}	ε_{2400}	FOM (W/cm^2)
$NiCo_2O_4$	0.91	0.30	0.95	0.858
$FeCo_2O_4$	0.80	0.17	0.81	0.759
$CoFe_2O_4$	0.82	0.20	0.66	0.784
$CuCo_2O_4$	0.89	0.22	0.82	0.847
$(NiFe)Co_2O_5$	0.88	0.34	0.70	0.837
SS304L coupon (no heat)	0.46	0.24	0.58	0.426
SS304L coupon	0.62	0.13	0.60	0.590

- $NiCo_2O_4$ shows high η_{sel}, due high α
  - However ε remains high
- Diffuse reflectance of some cobaltites show an undesirable absorptance “dip”, possibly due to a band gap transition
- $CoFe_2O_4$ does not have this dip and exhibits lower values of ε in the near-IR range
- Attempted to combine the high α of the cobaltite and the lower ε of the ferrites, several solid solutions were attempted
  - Some success in lowering ε versus $NiCo_2O_4$, but α was also lowered

Results-Electrodeposition



PXRD on thin films Co_3O_4/SS304L indicating the formation of the spinel (blue) phase directly. Strong peaks from the SS304L substrate are also observed (green).



Diffuse reflectance UV-Vis spectra of a) three Co_3O_4/MS-SS304L-P formed directly from high temperature electro-deposition.

- New high temperature electrodeposition method results in direct deposition of Co_3O_4 w/o need for additional sintering step
- Initial η_{sw} (0.849-0.871) look promising compared to Pyromark® 2500 (0.892)
- Amorphous phase may be present
  - Annealing studies (followed by XRD and SEM) will be performed to compare with previous ED results and to detect any change in crystallinity
- Mechanical stability seems improved on as-deposited coatings vs. rt deposition

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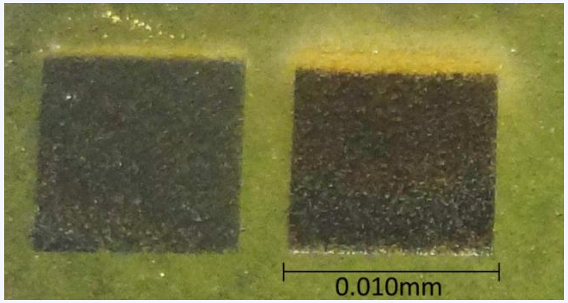
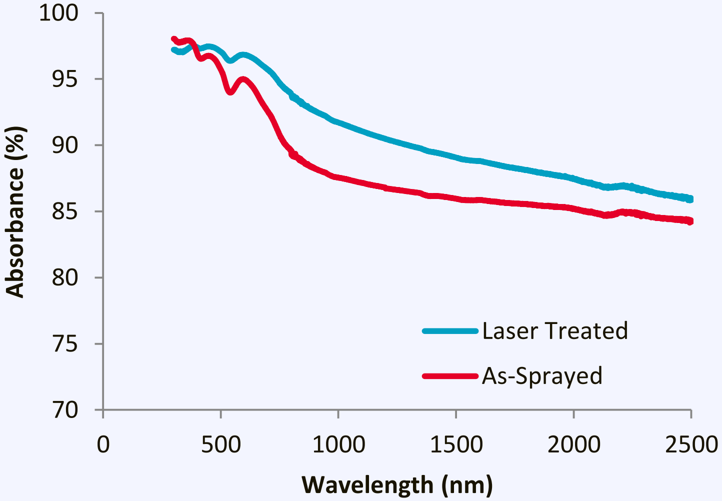
Results-Surface Modification of Thermal Sprayed Cr_2O_3

Cr_2O_3

- Melts at 2435 °C
- Extreme
  - –thermal stability
  - –chemical stability
  - –hardness
  - –wear resistance
- η_{sel} = 0.83 (as-deposited)



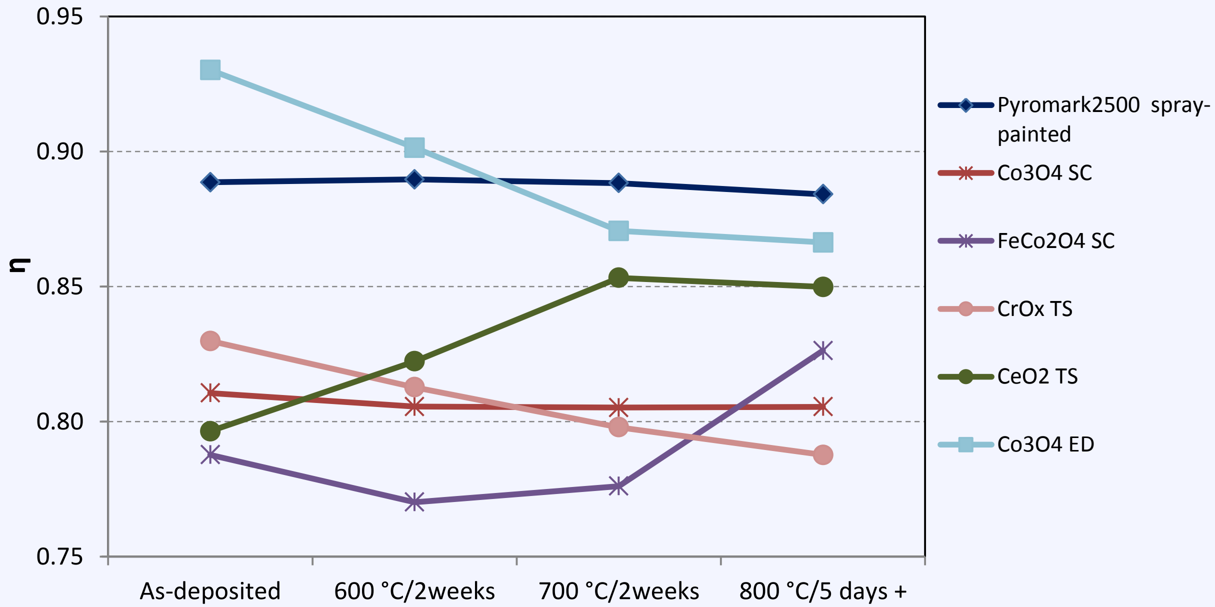
Microscopy image of Cr_2O_3 coating after laser surface treatment.



- Laser surface treatment has significantly darkened the coating
- Because of the small size of these treated areas it was not possible to acquire ε and α to determine η_{sel}
- Diffuse reflectance shows a measureable increase in absorbance post-laser treatment
- The mechanism for this change in reflectance is under investigation

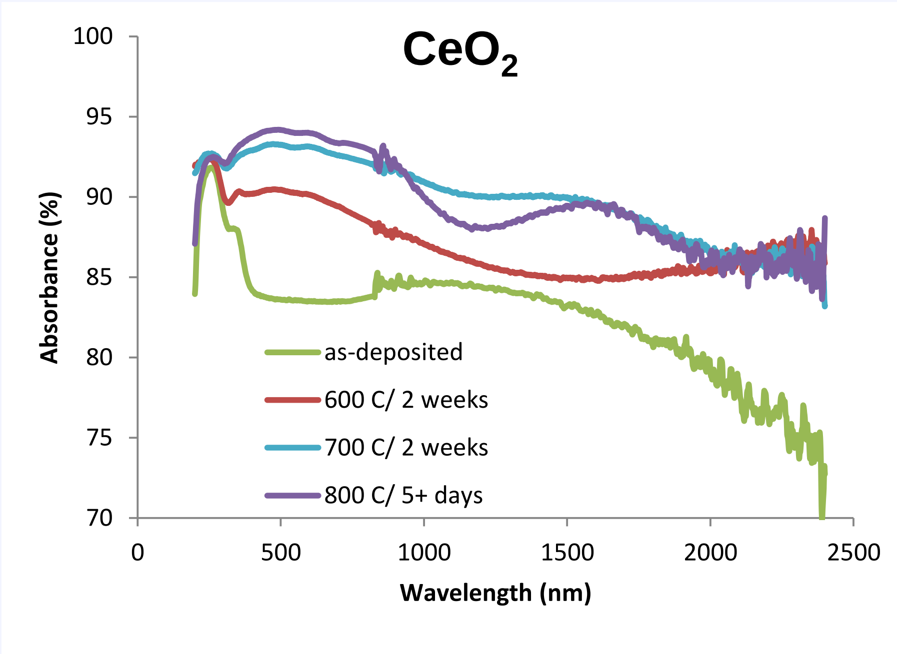
Results-Durability

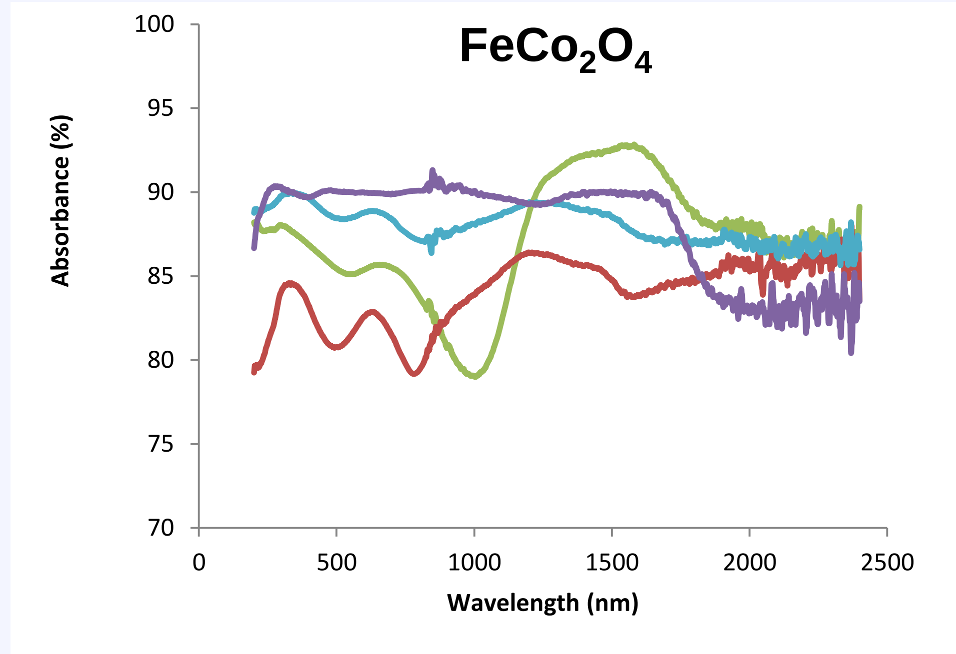
- Several coatings with high η were aged at various temperatures to investigate durability: 600 ºC for 2 weeks, 700 ºC for 2 weeks, and 800 ºC for 5+ days
  - Heating time for 800 ºC differs due to a furnace failure
- Pyromark® 2500 remains stable during aging, though α begins to decline after heating at 800 ºC heating
- Electrodeposited (rt) Co_3O_4 samples decline in performance, but remain competitive with Pyromark ®
  - However these films are not mechanically robust



FOM, η, for various coatings as a function of aging.

Results-Durability

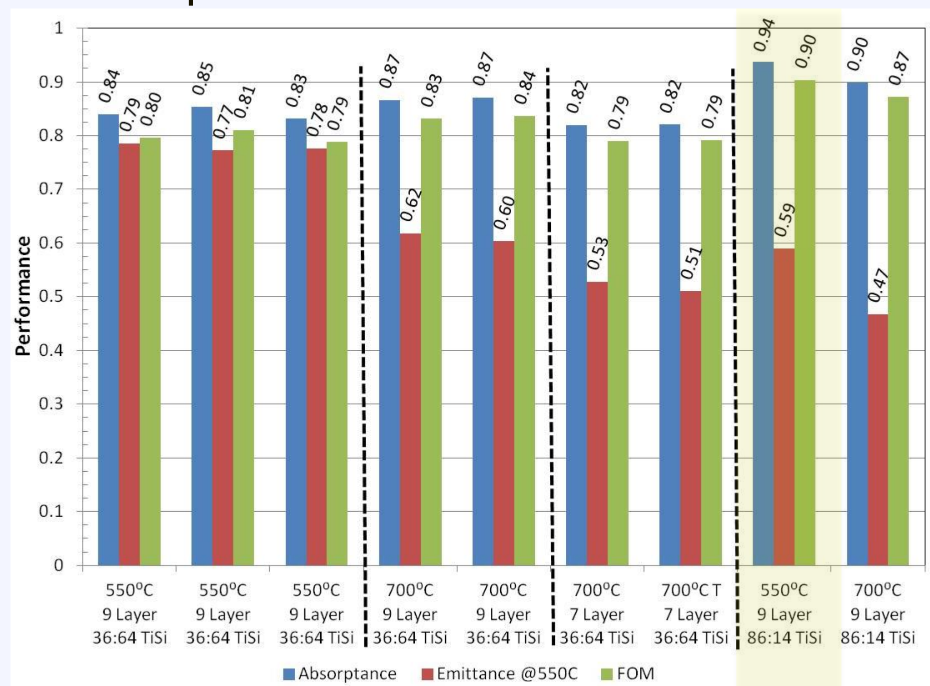




- Thermal sprayed CeO_2 coating actually increases in η_{sel} when aged
  - Visible darkening of coating, increase in α
    - Possibly reduction of the CeO_2 to $CeO_{2-\delta}$
    - Appearance of dip near 1200 nm after 800 ºC may imply formation of a band gap
  - Inadvertent doping via cation migration from the stainless steel substrate may also influence the coating properties of CeO_2
- Conversely, the dip present in as-deposited $FeCo_2O_4$ disappears upon heating
  - Increase in α, decrease in the near-IR range

Results-Sputtered TiSi Multilayers

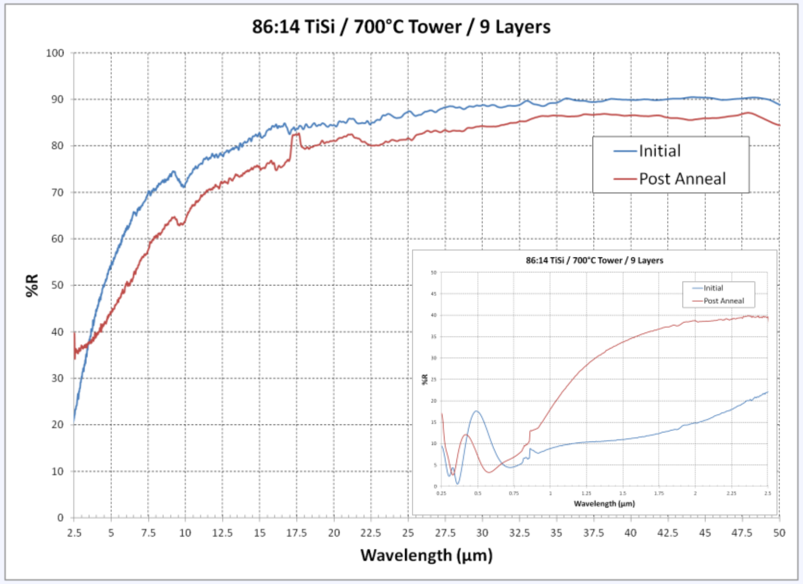
- Multi layer designs based on optical modeling with Essential Macleod™ were sputtered at NREL
  - Two Ti:Si compositions were chosen based on predicted stability from phase diagram: 36:64 and 86:14
  - Model anticipated critical wavelengths for 550 and 700 °C operation
  - Room temperature deposited coatings are amorphous
- Sputtered results:
  - Highest absorption = 0.94
  - Lowest 550 °C emittance = 0.47
  - 9 layer designs had better performance
  - 86:14 TiSi composition had better as-deposited performance
  - Initial TiSi η_{sel} > Pyromark™ at T >500 °C

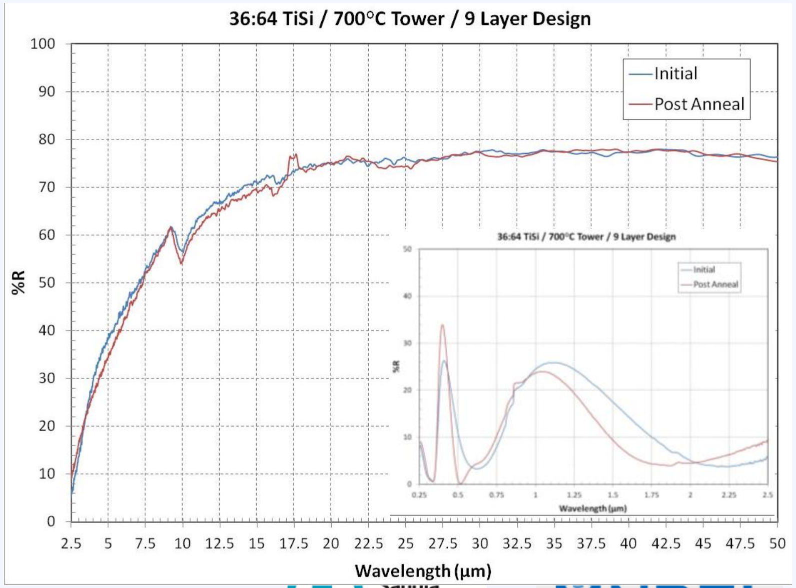


Multilayer absorber

Results- High Temperature Annealing

- Annealing screening experiments to determine appropriate temperature and gas mixture conditions
  - Heated to 550, 700, 900, and 1100 °C
  - Run under air, Ar, vacuum, forming gas
  - XRD and reflectance measurements
- Amorphous material shows partial crystallization to anticipated C-54 crystal structure
  - 86:14 TiSi composition materials showed the most conversion but adhesion and optical performance suffered
  - 36:64 TiSi composition remained more stable





Levelized Cost of Coating (LCOC)

- Similar to the levelized cost of electricity (LCOE)
- Defined as the ratio of the total annualized coating costs ($) to the annual thermal energy absorbed (kWh_{th}):

$$LCOC = C_{annual}/E_{thermal}$$

– C_{annual} = Initial coating cost/life of plant + recoating costs/recoating interval + lost revenue due to down time/recoating interval + annualized lost revenue due to degradation

– $E_{thermal}$ = Annual thermal energy absorbed (new) – Lost energy absorbed due to degradation – Lost energy absorbed due to recoating down time (annualized)

These parameters depend not only on the selective absorber efficiency, η_{sel}, which impacts the thermal energy absorbed and revenue costs, but also on degradation rate, material costs, and reapplication costs

Q1 Key Results and Outcomes

- High-temperature electrodeposition used to deposit Co_3O_4 coatings directly onto stainless steel coupons
  - Coatings show a figure of merit competitive with Pyromark©
- Thermal durability examination (600-800 °C) of coatings underway
  - Spin-coated and thermal-sprayed coatings remain robust
  - Most materials show a decline in optical properties, except for CeO_2 and $FeCo_2O_4$
- Thermal-sprayed Cr_2O_3 coatings were laser-treated to change surface morphology
  - Initial results show an increase in absorptance after treatment
- The 550 °C and 700 °C modeled multilayer Ti:Si stacks were deposited based on optimized single layer deposition conditions
  - As-deposited 84:16 Ti:Si composition competitive with Pyromark, but properties decline upon annealing
  - 36:64 stable under annealing conditions
- Levelized cost of coating (LCOC) (a LCOE-like metric) defined as the ratio of the total annualized coating costs ($) to the annual thermal energy absorbed (kWh_{th})

Future Work

- Quantify parameters (doping concentrations, thickness, deposition methods, substrate choice, and synthesis conditions) which yield optimized solar selective properties for spinels and thermally sprayed coatings
- Structural characterization to quantify changes in optical properties of annealed and surface-modified coatings
- Downselect to five candidate binary materials for PVD of a full-stack whose modeled properties have a selective absorber efficiency that meet or exceeds η_{sel}=0.916
- Document the system-level LCOC metric for candidate selective surface coatings and Pyromark which incorporates initial and reoccurring costs (materials, labor, and equipment) along with performance

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Questions?