

# High Temperature Solar Selective Coatings for Solar Power Central Receivers

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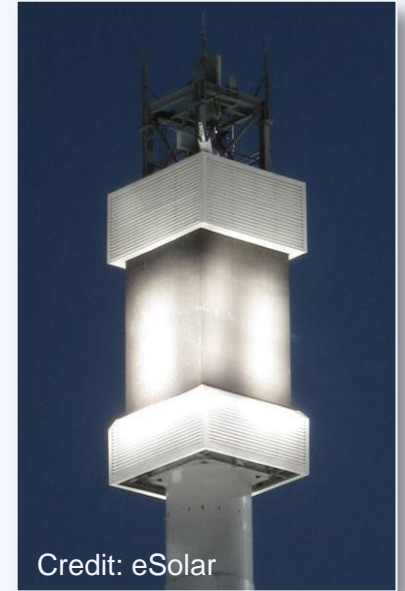
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**Sandia National Laboratories**

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Session1-14-6: Receiver Modeling and Thermal Storage Analysis

# Project Description

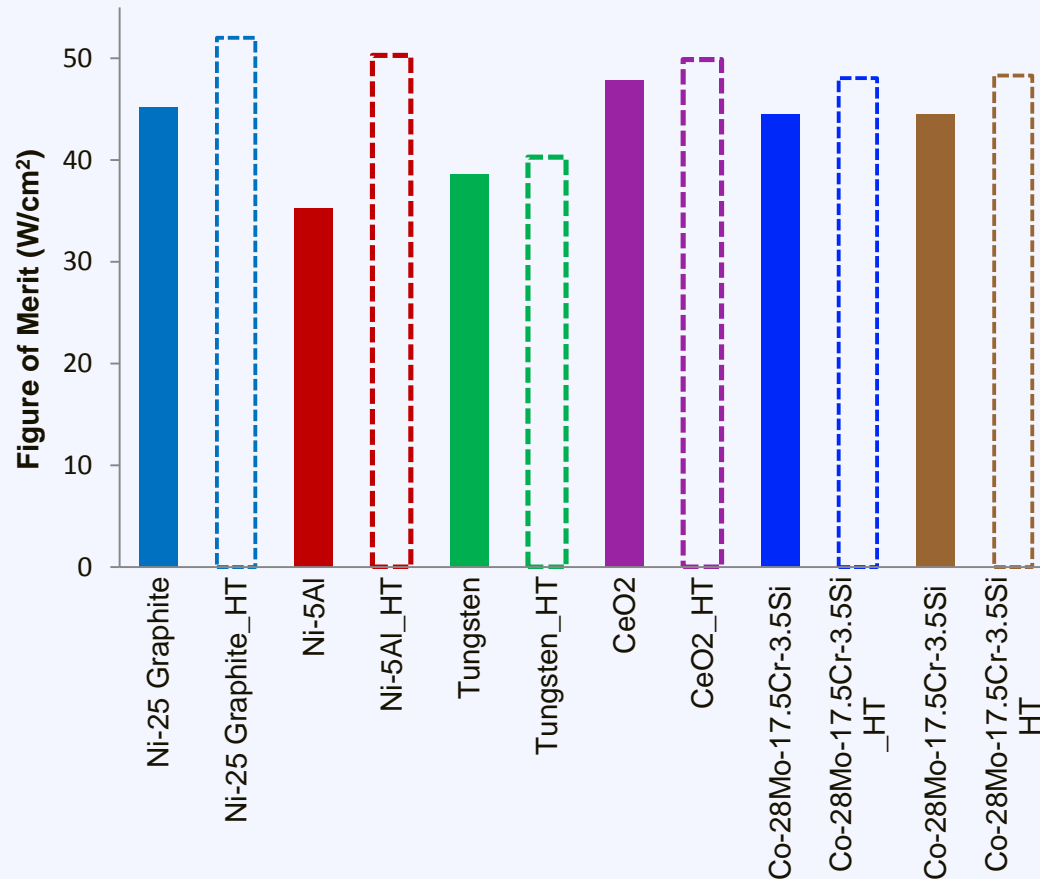
- Next-generation power tower temperatures will likely operate at temperatures  $\geq 650\text{ }^{\circ}\text{C}$
- The efficiency of a power tower plant can be increased if the energy absorbed by the receiver is maximized while the heat loss from the receiver to the environment is minimized
- Pyromark® has a high solar absorptance ( $\alpha > 0.95$ ), but also high emittance ( $\varepsilon \sim 0.87$ ) 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  $> 500\text{ }^{\circ}\text{C}$



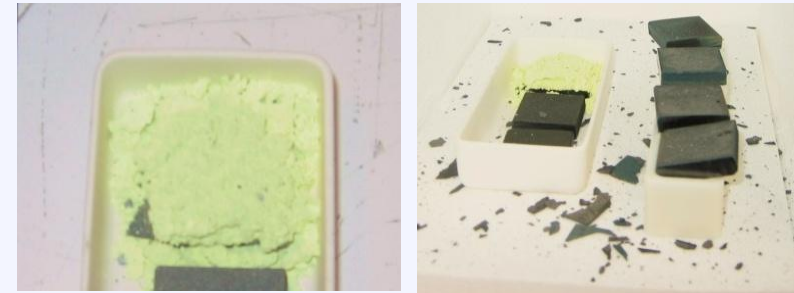
*Improved selective absorber coatings for receivers must maintain high absorptance in the solar spectrum but lower emittance in the infrared spectrum. It must also be stable in air, easily applied at large scales, cost effective, and survive thousands of heating and cooling cycles*

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

# Heat Treated Coatings



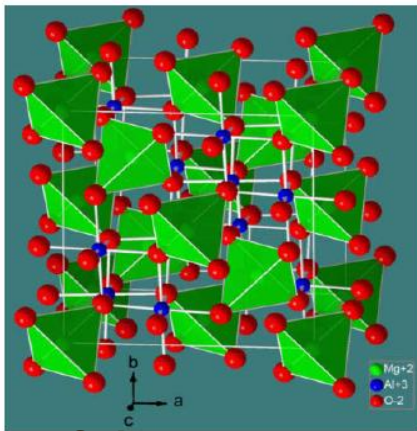
FOMs for as-deposited (filled bars) coating test coupons and coating test coupons heat treated for 6 hours at 600° C (open bars).



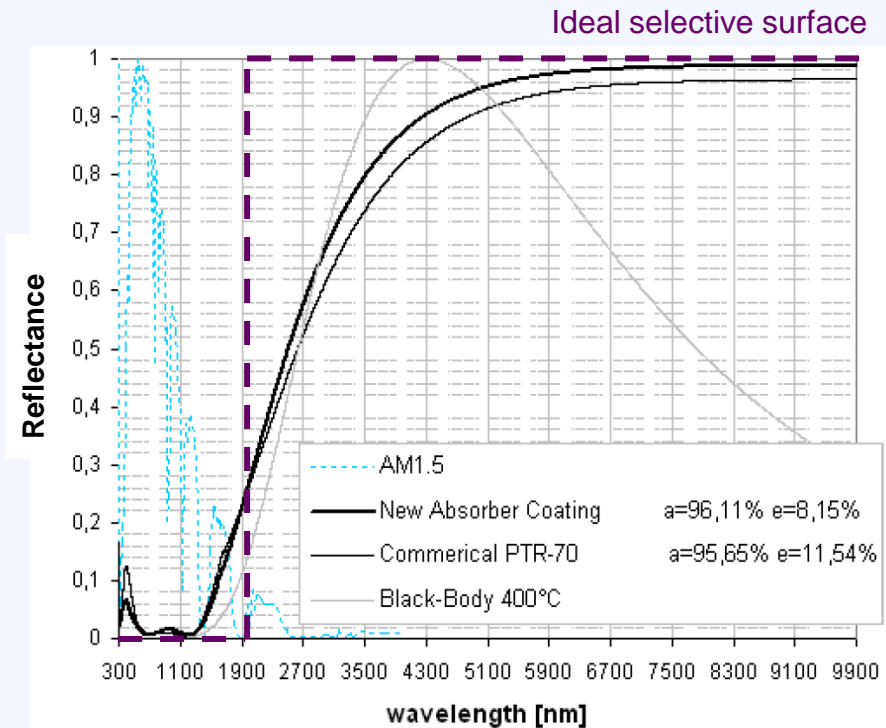
- Heating generally increased both  $\alpha$  and  $\epsilon$ , resulting in an overall increase in FOM
- Likely surface oxidation
  - Sometimes results in violent oxidation (tungsten) or spalling (tungsten carbide)
  - Effects thermal stability of films
- Surface modification (smoothing) may also occur over time; under investigation

# Materials

- Novel materials that are intrinsically solar selective: high  $\alpha$ , low  $\epsilon$  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



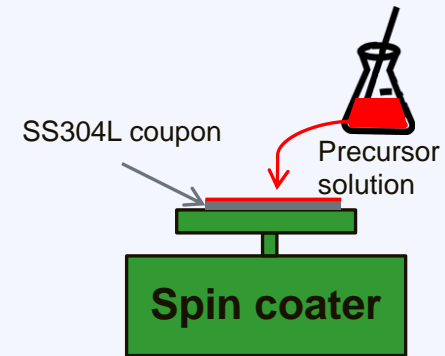
Spinel structure



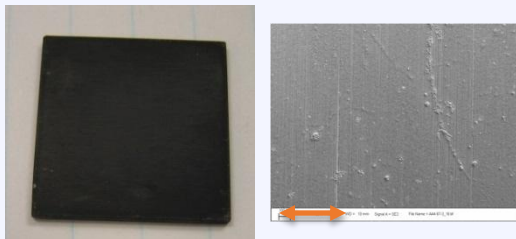
N. Benz, et al, Advances In Receiver Technology For Parabolic Troughs, SolarPACES 2008.

# 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

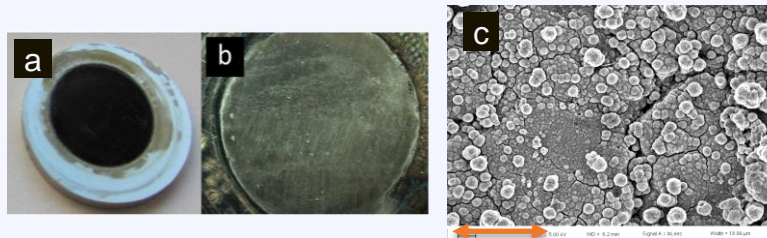


Spin coating (top) and electrodeposition (bottom)



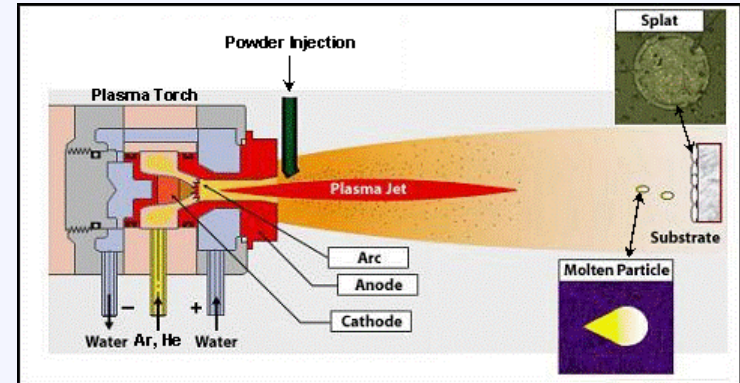
$\text{FeCo}_2\text{O}_4$  coating (left) and SEM of  $\text{FeCo}_2\text{O}_4$  surface (right). Scale bar = 500  $\mu\text{m}$ .

- (a)  $\text{Co}_3\text{O}_4/\text{SS304L}$  prepared high-T ED method (middle).  
 (b) Image of  $\text{Co}_3\text{O}_4$  film (deposited for 4h) on SS304L.  
 (c) SEM image is shown at far right (scale bar = 5  $\mu\text{m}$ )



# 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



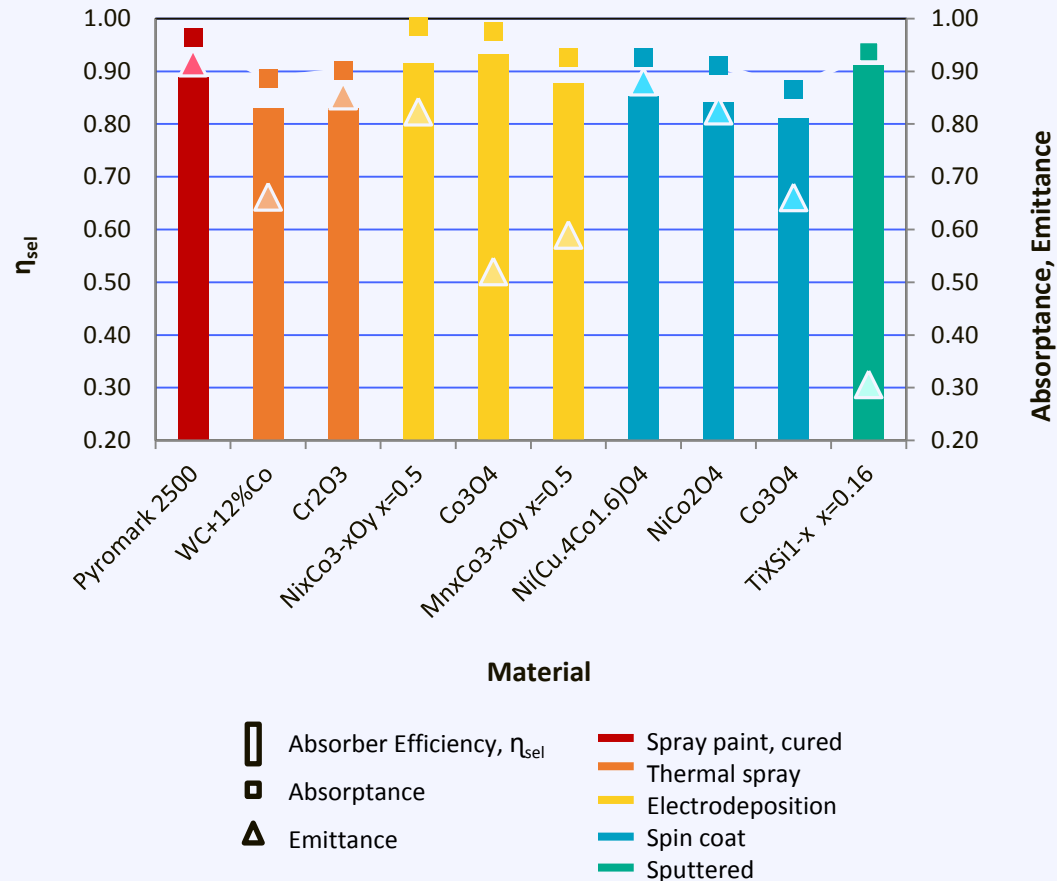
Air-plasma thermal spraying process for absorber coatings



# Figure of Merit, $\eta_{sel}$

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

- $\alpha_s$  = solar absorptance
- $Q$  = irradiance on the receiver ( $\text{W/m}^2$ )
- $\varepsilon$  = thermal emittance
- $\sigma$  = Stefan-Boltzmann constant ( $5.67 \times 10^{-8} \text{ W/m}^2/\text{K}^4$ )
- $T$  = surface temperature (K)



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

# 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 ( $\text{kWh}_{\text{th}}$ ):

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

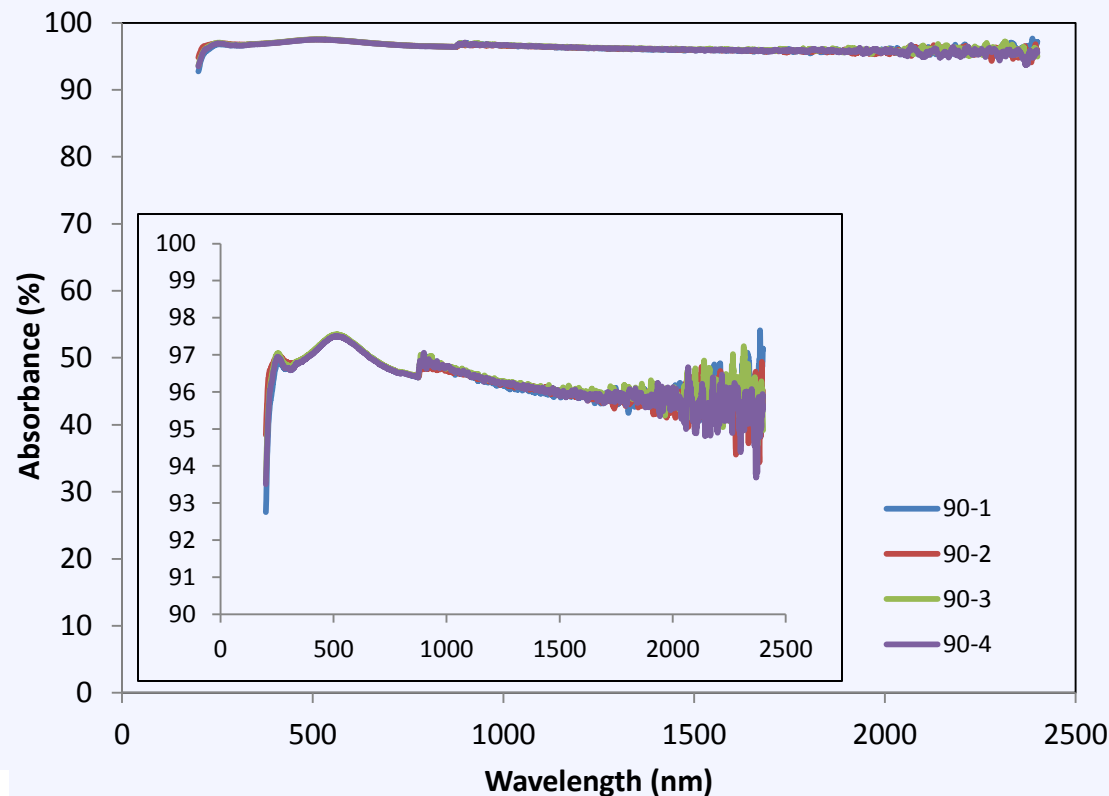
- $C_{\text{annual}}$  = Initial coating cost/life of plant + recoating costs/recoating interval + lost revenue due to down time/recoating interval + annualized lost revenue due to degradation
- $E_{\text{thermal}}$  = Annual thermal energy absorbed (new) – Lost energy absorbed due to degradation – Lost energy absorbed due to recoating down time (annualized)

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

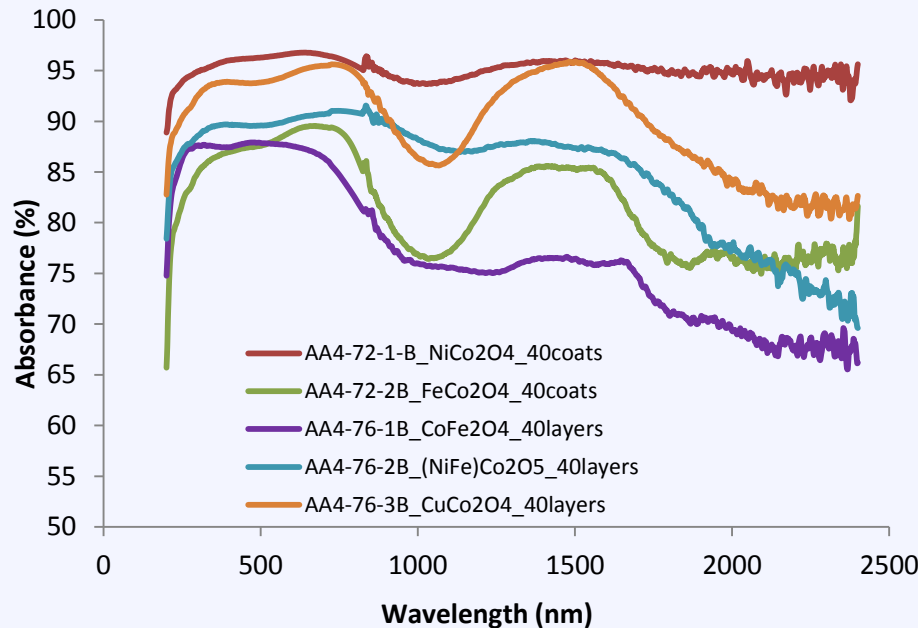


# Pyromark 2500

Sample	$\alpha$ (solar)	$\epsilon$ (80C rel)	$\epsilon$ (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



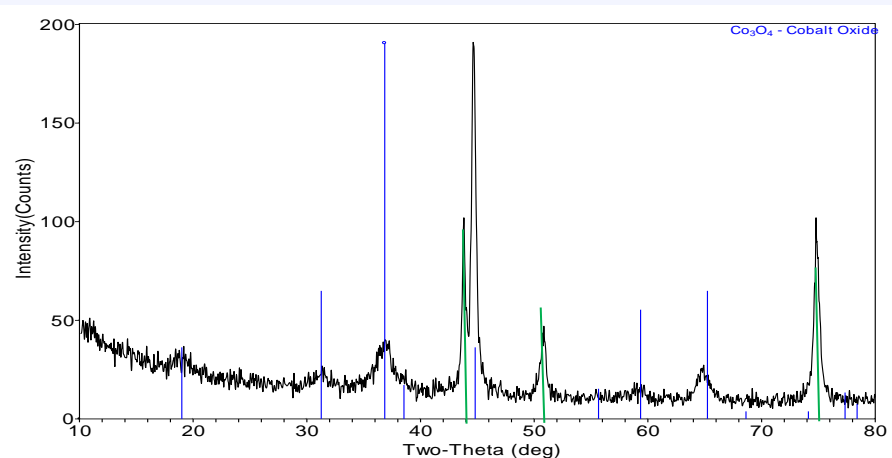
# Results-Spin Coated Films



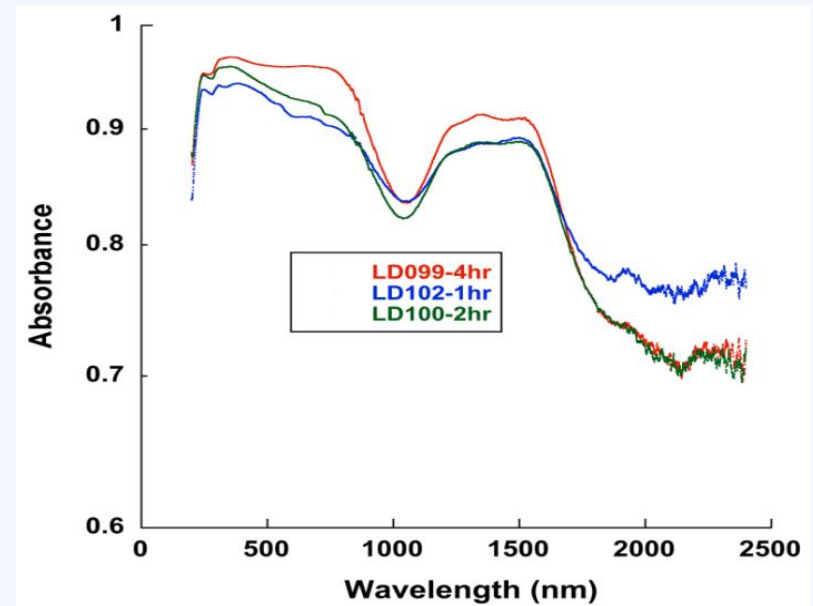
- $\text{NiCo}_2\text{O}_4$  shows high  $\eta_{\text{sel}}$ , due high  $\alpha$ 
  - However  $\epsilon$  remains high
- Diffuse reflectance of some cobaltites show an undesirable absorptance “dip”, possibly due to a band gap transition
- $\text{CoFe}_2\text{O}_4$  does not have this dip and exhibits lower values of  $\epsilon$  in the near-IR range
- Attempted to combine the high  $\alpha$  of the cobaltite and the lower  $\epsilon$  of the ferrites, several solid solutions were attempted
  - Some success in lowering  $\epsilon$  versus  $\text{NiCo}_2\text{O}_4$ , but  $\alpha$  was also lowered

Material	$\alpha$	$\epsilon_{80}$	$\epsilon_{2400}$	FOM (W/cm <sup>2</sup> )
$\text{NiCo}_2\text{O}_4$	0.91	0.30	0.95	0.858
$\text{FeCo}_2\text{O}_4$	0.80	0.17	0.81	0.759
$\text{CoFe}_2\text{O}_4$	0.82	0.20	0.66	0.784
$\text{CuCo}_2\text{O}_4$	0.89	0.22	0.82	0.847
$(\text{NiFe})\text{Co}_2\text{O}_5$	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

# Results-Electrodeposition



PXRD on thin films Co<sub>3</sub>O<sub>4</sub>/SS304L indicating the formation of the spinel (blue) phase directly. Strong peaks from the SS304L substrate are also observed (green).



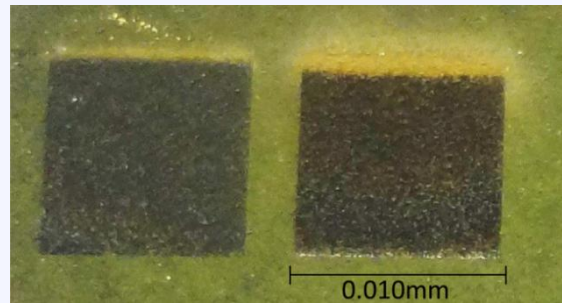
Diffuse reflectance UV-Vis spectra of a) three Co<sub>3</sub>O<sub>4</sub>/MS-SS304L-P formed directly from high temperature electro-deposition.

- New high temperature electrodeposition method results in direct deposition of Co<sub>3</sub>O<sub>4</sub> w/o need for additional sintering step
- Initial  $\eta_{sw}$  (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

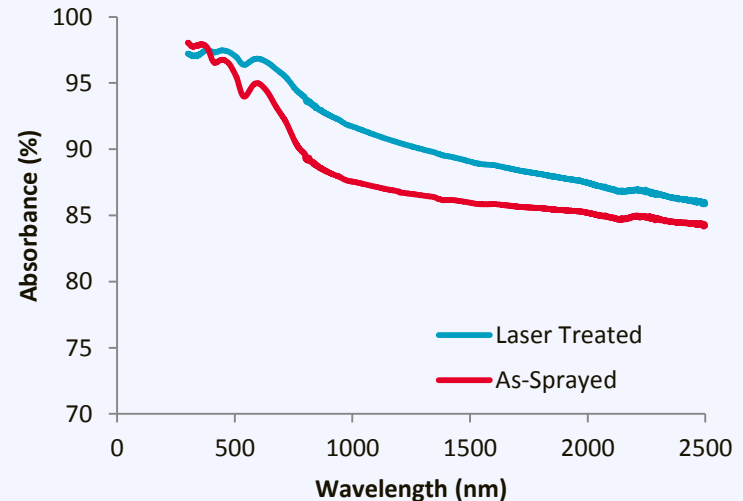
# Results-Surface Modification of Thermal Sprayed $\text{Cr}_2\text{O}_3$

## $\text{Cr}_2\text{O}_3$

- Melts at 2435 °C
- Extreme
  - thermal stability
  - chemical stability
  - hardness
  - wear resistance
- $\eta_{\text{sel}} = 0.83$   
(as-deposited)



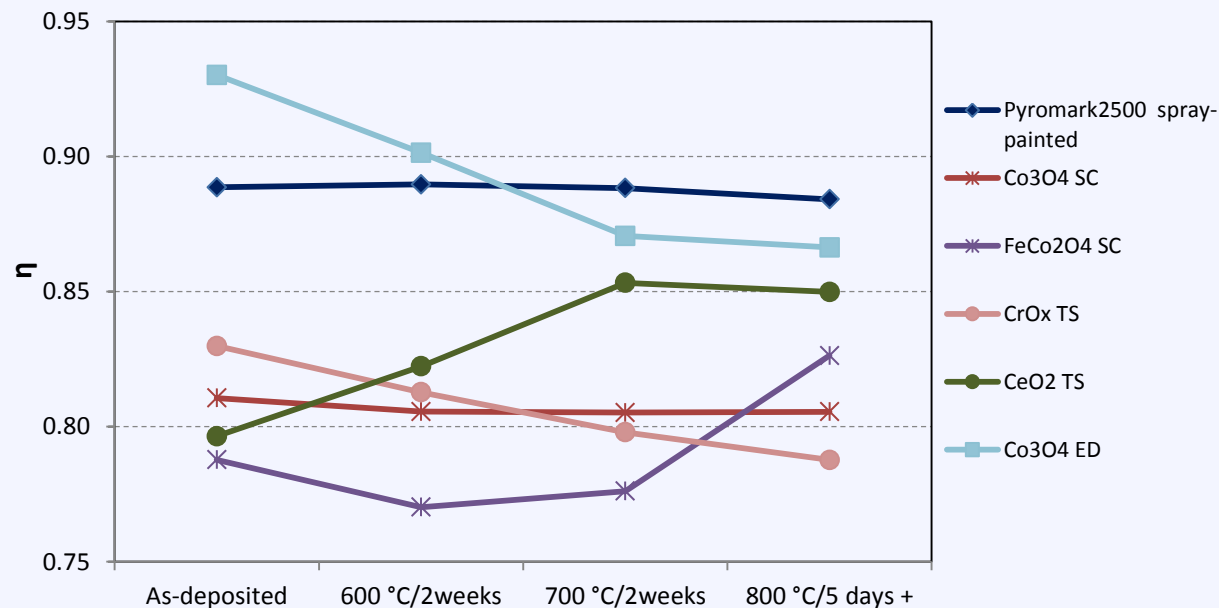
Microscopy image of  $\text{Cr}_2\text{O}_3$  coating after laser surface treatment.



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

# Results-Durability

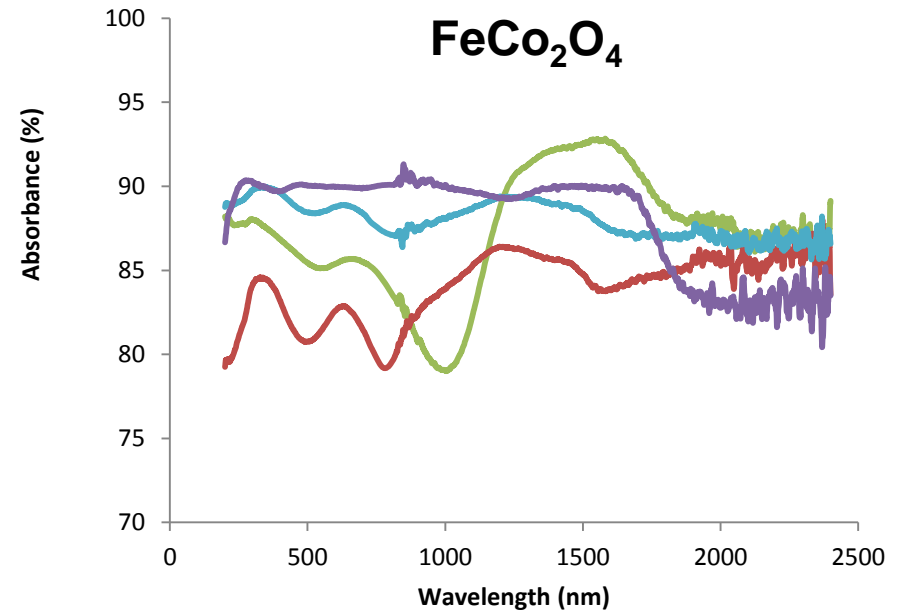
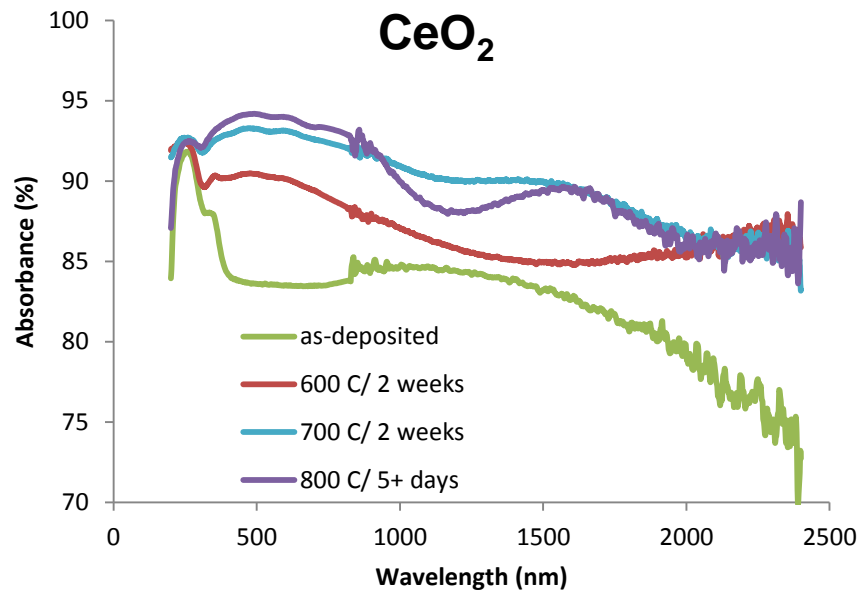
- Several coatings with high  $\eta$  were aged at various temperatures to investigate durability: 600 °C for 2 weeks, 700 °C for 2 weeks, and 800 °C for 5+ days
  - Heating time for 800 °C differs due to a furnace failure
- Pyromark<sup>®</sup> 2500 remains stable during aging, though  $\alpha$  begins to decline after heating at 800 °C
- Electrodeposited (rt)  $\text{Co}_3\text{O}_4$  samples decline in performance, but remain competitive with Pyromark<sup>®</sup>
  - However these films are not mechanically robust



FOM,  $\eta$ , for various coatings as a function of aging.

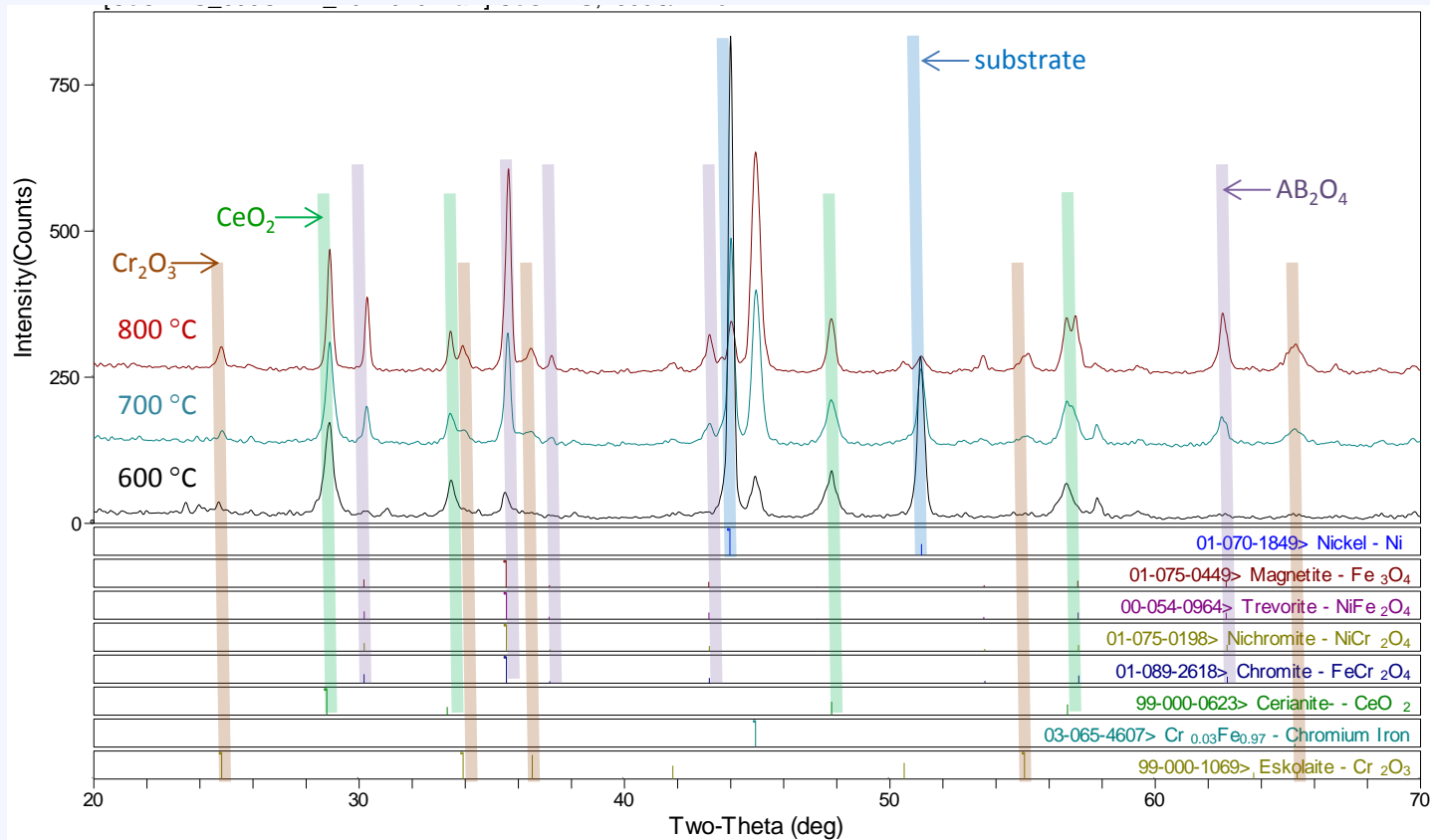
Ambrosini, ASME ES2013

# Results-Durability



- Thermal sprayed  $\text{CeO}_2$  coating actually increases in  $\eta_{\text{sel}}$  when aged
  - Visible darkening of coating, increase in  $\alpha$ 
    - Possibly reduction of the  $\text{CeO}_2$  to  $\text{CeO}_{2-\delta}$
    - Appearance of dip near 1200 nm after 800 °C may imply formation of a band gap
  - Inadvertent doping via cation migration from the stainless steel substrate may also influence the coating properties of  $\text{CeO}_2$
- Conversely, the dip present in as-deposited  $\text{FeCo}_2\text{O}_4$  disappears upon heating
  - Increase in  $\alpha$ , decrease in the near-IR range

# Durability of $\text{CeO}_2$



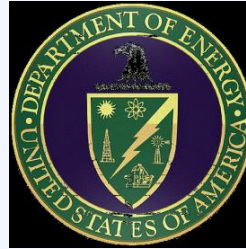
- Peaks corresponding to  $\text{CeO}_2$  change little with heating, but
- Peaks corresponding to the substrate (“Ni”) decrease, while those corresponding to “ $\text{AB}_2\text{O}_4$ ” and oxidized Cr increase with temperature
  - Phase likely forms upon the oxidation of the stainless steel substrate
- Either of these phases, which are more absorptant than ceria, may account for the increase in absorptivity.



# Summary

- High-temperature electrodeposition used to deposit  $\text{Co}_3\text{O}_4$  coatings directly onto stainless steel coupons
  - Coatings show a figure of merit competitive with Pyromark<sup>®</sup>
- 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  $\text{CeO}_2$  and  $\text{FeCo}_2\text{O}_4$
  - Reaction with substrate at higher temperatures remains a concern
- Thermal-sprayed  $\text{Cr}_2\text{O}_3$  coatings were laser-treated to change surface morphology
  - Initial results show an increase in absorptance after treatment
- 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 ( $\text{kWh}_{\text{th}}$ )

# Acknowledgements



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# Thank you for your attention. Questions?

