SunShot
U.S. Department of Energy

CSP Program Summit 2016

High-Temperature Solar Selective Coating Development for Power Tower Receivers

CSP: LDPD_Ambrosini_A
Duration: 3 years (ending Dec. 2015)
DOE Funding: $2,517,000

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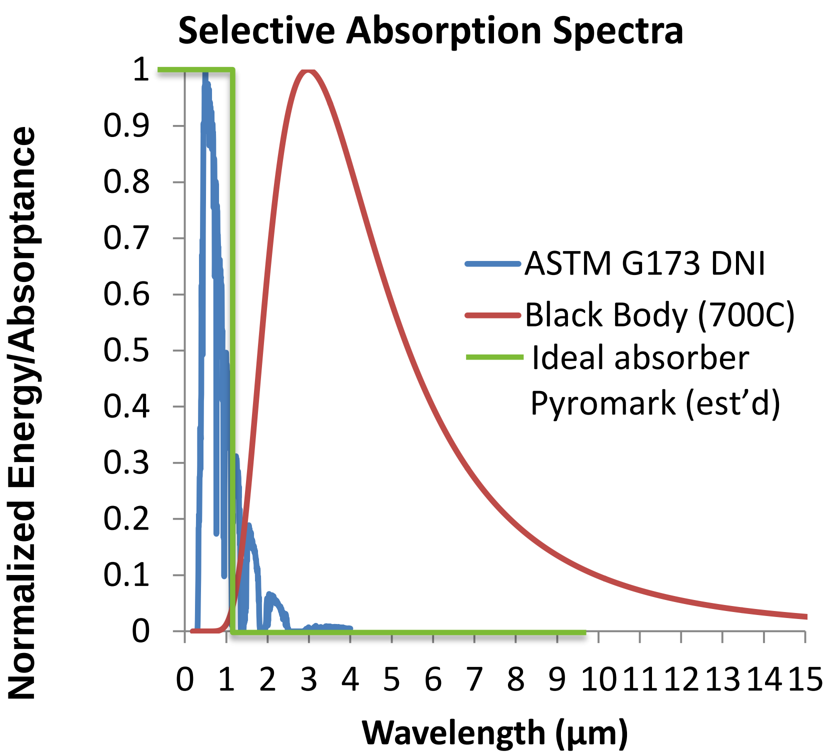
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND Number: 2014-3715P.

Problem Statement

To meet the SunShot goal of Levelized cost of energy (LCOE) ≤ 6¢/kW$_h$ by 2020, next generation power towers will operate at temperatures > 600 °C in order to take advantage of increased efficiencies of high-temperature operation. Current receiver coatings, such as Pyromark 2500, while highly absorptant, suffer from high emittance and have been reported to degrade during operation at T > 600 °C . Advanced solar selective absorber (SSA) coatings are required *that have a solar efficiency, η, surpassing that of Pyromark® 2500, are stable at ≥ 600 ºC in air, have high thermal conductivity, and are nonvolatile.*



Value Proposition

An increase in the thermal efficiency of SSZ coatings by 4% at 650 ℃, and 7% at 800 ℃, can potentially reduce the LCOE by an estimated 0.25 ¢/kWh.

Formulations of mixed-metal oxides, such as spinels (AB_2O_4) and perovskites (ABO_3), are promising candidates for next-gen receiver coatings. They are stable at high-temperatures, oxidation resistant, can be easily deposited via techniques such as thermal spray, and are amenable to cation doping and substitution to chemically tailor their properties. Refractory metal silicides (MSi_x) are another class of materials that display inherently high absorptance and low emittance in multilayer SSA coatings. Both families are reported herein.

Deposition Methods

Spin Coating	Electrodeposition	Thermal Spray	Physical Vapor Deposition
Facile synthesis of coatings with varying formulations and dopant concentrations	Novel approach to screening solar selective materials	High-surface area coating technique	Fine control of deposition conditions
Allows for rapid deposition and optical screening of a composition space	Can result in unusual surface morphologies	Ability to coat in the field	Control of optical, microstructural, & mechanical properties
		Can modify surface morphology in an efficient and cost-effective manner	Pulsed DC sputtering is commercial method used for receiver tubes

A complimentary suite of coating techniques to investigate novel formulations, surface morphology, layered structures and scale-up.

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Project Objectives

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

Milestones - Sandia

MS	Description	% Complete
1.1	Quantify parameters (doping concentrations, thickness, deposition methods, substrate choice, and synthesis conditions) which yield optimized solar selective properties for spinels and thermally sprayed coating and meet or exceed the selective absorber efficiency of best formulations from FY12 AOP (e.g., Co3O4-based spinels,$\eta_{sel}=0.916$) and present to DOE statistical method used and results.	100%
1.3	Complete SAND report documenting the system-level metric for candidate selective surface coating and Pyromark which incorporates initial and reoccurring costs (materials, labor, and equipment) along with performance.	100%
2.1.1	Determine acceptable material performance based on selective absorber efficiency vs. degradation rate for a given reapplication interval.	100%
2.1.2	Identify at least one successful candidate coating. A successful coating will exhibit a calculated LCOC less than that of Pyromark, which is currently estimated at $0.055/MWht.	75%
2.2.1	Utilize results of Gibbs free energy modeling to predict potential secondary phase reaction between substrates and coatings. Apply results to identification of by-products during heating tests, and determine if the model effectively predicts phase formation (within 80%), thus allowing us to assess the effectiveness of such calculations as a tool for predicting substrate-coating interaction.	0%
2.2.2	Produce at least one coating with a solar selective efficiency of $\eta_{sel} > 0.911$ under similar conditions.	95%
2.2.3	Utilize isothermal measurements calculate degradation rates of the coatings. From these data, reapplication intervals and performance can be estimated. Candidate materials that fall within the shaded region of Fig. 1 will be considered promising.	90%
2.2.4	Evaluate mechanical durability of coatings after high temperature exposure using an appropriate adhesion test method.	50%
2.2.5	Utilize characterization results to identify types and possible causes of performance degradation in coatings. Depending on the type and extent of the degradation, solutions such as applying a barrier coating to resist cation diffusion or an AR top layer to prevent surface sintering can be investigated as remediation techniques.	90%
2.3.1	Build and test the on-sun test rig. Validate its performance by running a test matrix on Pyromark 2500 and comparing it with previous data taken on the Pyromark material to see if the results track to within 90% with previously published observations of Pyromark performance.	100%
2.3.2	Document performance (absorbed power, efficiency, durability) and characterization (optical and structural) of candidate coatings under solar conditions representative of CSP receiver operating conditions, (e.g., thermal conditions representing >500 kW/m2, ≥700°C, on-sun/off-sun cycling). Utilize data to further elucidate degradation processes identified in Task 2.2 and to identify coatings that meet acceptable metrics identified by the LCOC	100%
2.3.3	Identify candidate coatings that exhibit less degradation on-sun than Pyromark 2500, which is currently reported to optically degrade at 0.5 %/yr and require a reapplication interval of 5 years	80%
3.1.0	Populate Milestone Table file "SNL_Ambrosini_Correlation Coefficients" with all those variables that could be of interest in the Phase 3 experiments. Next, we will compute the number of combinations for all the variables in the file. Finally, we will state what subset of these combinations will be evaluated in Phase 3.	100%
3.1.1	Parameters most influential to coating performance (η) of Pyromark are identified	100%
3.2.1	Identify deposition parameters that maximize η after testing (>200 cycle at >700 °C)	75%
3.3.1	Results from lab to field successfully translated	0%
3.3.2	Performance of coatings on Haynes tubes	20%
3.3.3	Disseminate results	0%

Milestones - NREL

MS	Description	Complete
1.2.1	Downselect 5 candidate binary materials for full stack	——
1.2	Preliminary Rank-order of materials and methods for refractory metal compounds based on η(sel) and thermal stability	——
2.1	Use plots of FOM vs roughness to determine range of adequate (>0.91) performance	
2.2	Determine full rankings of tested single layer materials and applied coating designs for refractory metal compounds based on their ability to produce efficiency better than ηsel = 0.910 and degradation of < 1%/yr	✓
2.3	Provide a rank ordering of the degradation rate of candidate samples at elevated temperatures in air as a function of hours of exposure. Identify at least two different base material coatings better than ηsel =0.910 after 400 hours of isothermal testing at 700 °C	--
2.4	Demonstrate control of intensity and temperature. Quantify performance, including uncertainties, for absorbed power, efficiency, and durability of candidate coatings under solar conditions representative of operating conditions (e.g., thermal conditions representing =500 kW/m2, =700 °C)	✓
2.5	Quantify spectral reflectance and resulting ηsel for coatings at selected temperatures as a function of time (e.g., 0, 100, 300 hours) and cycles (e.g., 0, 10, 100 cycles). Demonstrate at least one coating where ηsel after cycling is greater than 0.910 after a minimum of 50 cycles at 700 °C.	--
3.1.1	We will exhaustively populate Milestone Table file "NREL_Gray_Correlation Coefficients" with all those variables that could be of interest in the Phase 3 experiments. Next, we will compute the number of combinations for all the variables in the file.	✓
3.1.2	Embed the MS Word file "NREL_Gray_Correlation_Coefficients" containing the agreed to subset from milestone 3.1.1	✓
3.1.3	Comparison of absorptance spectrum (250 -1700 nm) for un-aged and 500 hour aged, simplified multi-layer samples (3 or more layers including each of the materials (TaSi2, SiO2 and TiO2) used in the full SSA design).	✓
3.1.4	Comparison of absorptance spectrum (250 -1700 nm) for un-aged, simplified multi-layer samples (3 or more layers including each of the materials (TaSi2, SiO2 and TiO2) used in the full SSA design) vs. modeled.	--
3.1.5	Comparison of absorptance spectrum (250 -1700 nm) for 500 hour aged, simplified multi- layer samples (3 or more layers including each of the materials (TaSi2, SiO2 and TiO2) used in the full SSA design)vs. modeled.	✓
3.1.6	Perform sensitivity analysis of material and/or layer impact on stack performance with variation in n, k and/or layer thickness according to observed bounds. Generate a hierarchy of influence. Focus initial efforts of establishing Correlation Coefficients (above) for primary influences.	——

Levelized Cost of Coating (LCOC)

Solar efficiency, η, evaluates the optical properties of a material, which impacts the thermal energy absorbed. LCOC also incorporates degradation rate, material costs, and reapplication costs resulting in a more comprehensive cost estimate.

Solar Efficiency, η

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

α_s = solar absorptance
Q = irradiance on the receiver
ε = thermal emittance
σ = Stefan-Boltzmann constant
T = surface temperature (K)

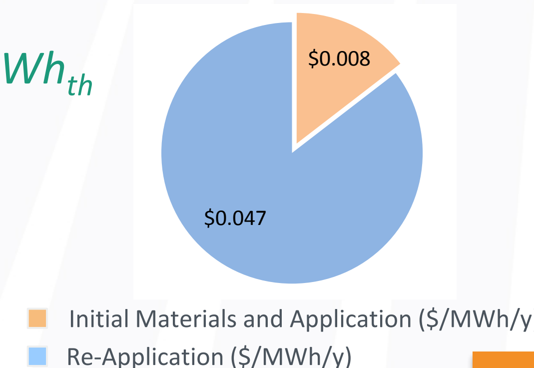
$LCOC_{marginal} = C_{annual}/E_{thermal}$

C_{annual} = Total annualized coating costs
= Initial coating cost/life of plant +
Recoating costs/ recoating interval +
Cost of additional (or fewer) heliostats to yield baseline power

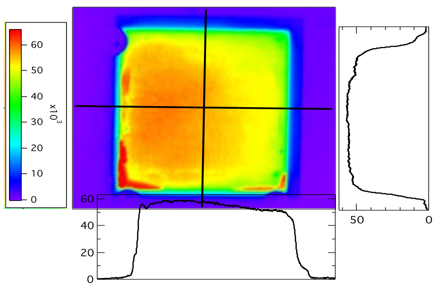
$E_{thermal}$ = Annual thermal energy absorbed (new) –
Lost energy absorbed due to degradation –
Lost energy absorbed due to recoating down time (annualized)

Annualized LCOC for Pyromark 2500 is $0.055/$MWh_{th}$

- Assumed 100 MW_e molten-salt power plant with a ~50% capacity factor
- η_{sel} = 0.89 (solar absorptance = 0.96, thermal emittance = 0.87)
- Assumed degradation rate of 0.5% per year
  - Degradation rates and costs for materials, application, and reapplication are based on available data from Solar One, Ho et al. (2012), and eSolar



Solar Testing Facilities



NREL: Solar furnace test stand
- Simultaneous measurement of multiple samples
- Uniform illumination of samples
- Minimal “cross-talk” between samples
- T ~700 °C at 500 kW/m^2
- Delivers 650 kW/m^2 over 4”x4” area

SNL: Solar furnace test stand
- Spot size: 6 inches
- Peak irradiance: 6 MW m^{-2}
- Average irradiance: 5 MW m^{-2}
- Operational hours/day: 6
- Air cooled

SNL: Solar simulator
- Spot size: 1 inch
- Peak Irradiance:1.3 MW/m^2
- Average Irradiance: 0.9 MW/m^2
- Operational: 24/7
- Automatic, robotic sample holder for multiple sample testing

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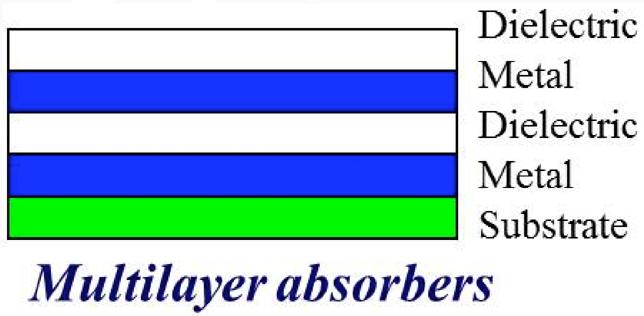
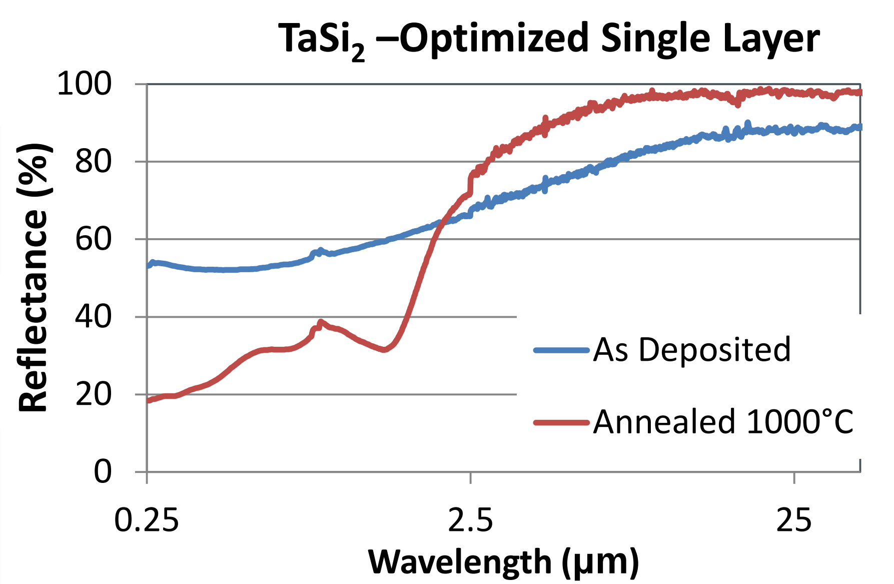
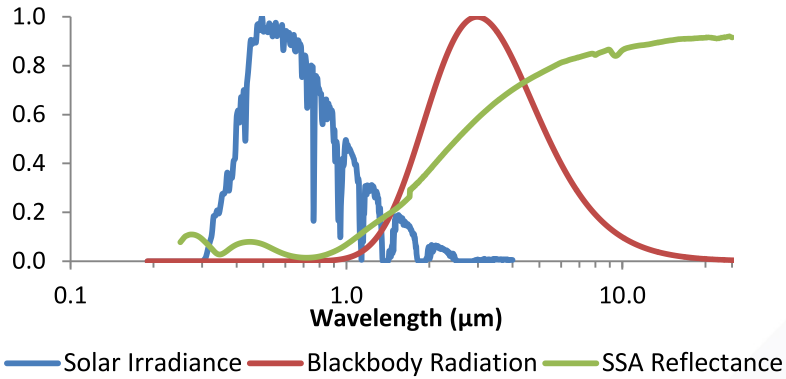
$TaSi_2$-Based Solar Selective Absorber

- $TaSi_2$ material properties from previous modeling activities indicated potential application for multilayer SSA
- Crystallization of monolayer $TaSi_2$ further improved optical properties
  - Increased IR reflectance (low emittance)
  - Increased absorption in UV-Vis-NIR
  - α_s >0.94 and η_{sol} >0.91
- Stack design optimized for material and operating conditions



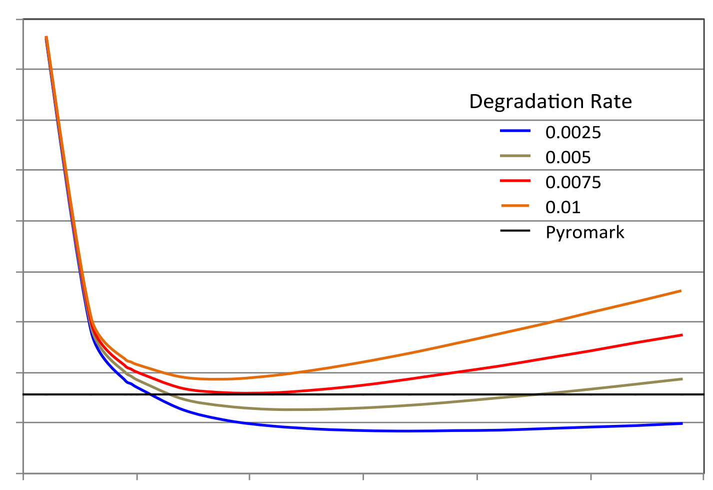


Selective Absorber Efficiency

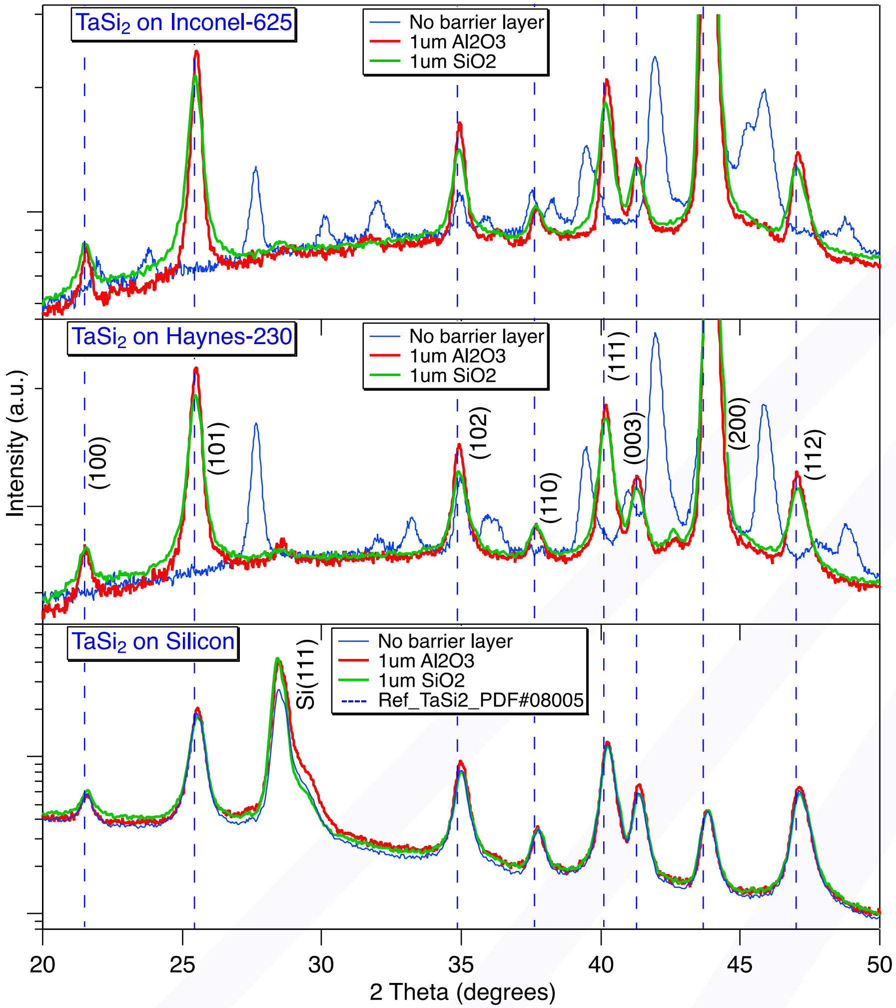


Design/Material	“9”	Pyromark
Solar Absorptance (%)	0.945	0.962
ε_{700}	0.373	0.847
Irradiance (W/cm²)	η_{abs} (700 °C)	
10	0.755	0.532
20	0.850	0.747
30	0.882	0.819
40	0.897	0.854
50	0.907	0.876
60	0.913	0.890
70	0.918	0.901
80	0.921	0.908
90	0.924	0.914
100	0.926	0.919

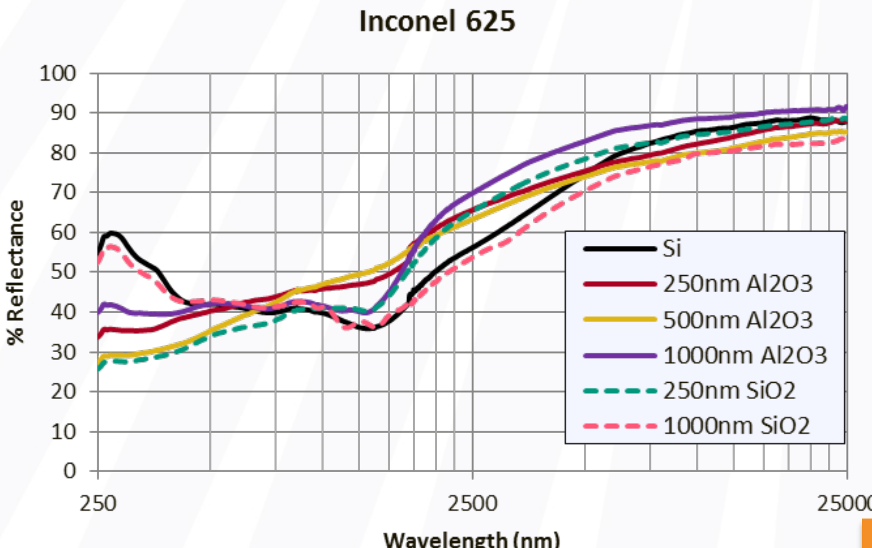
- $TaSi_2$ SSA shows better efficiency than Pyromark across full irradiance spectrum at 700 °C
- LCOC shows benefit with annual degradation rates < 0.0075 η / yr



Barrier Layers

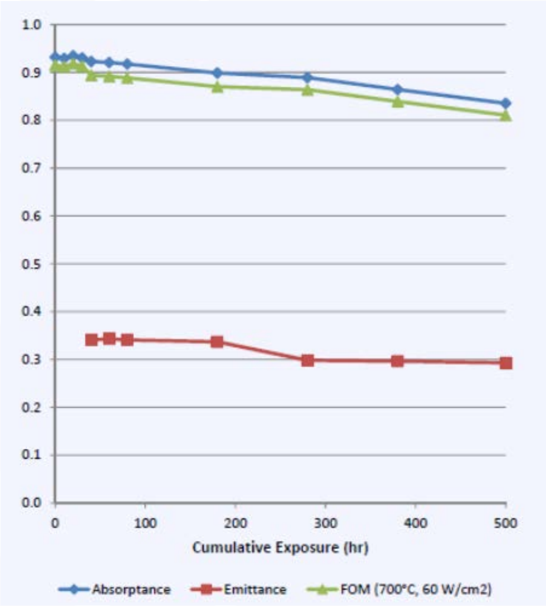


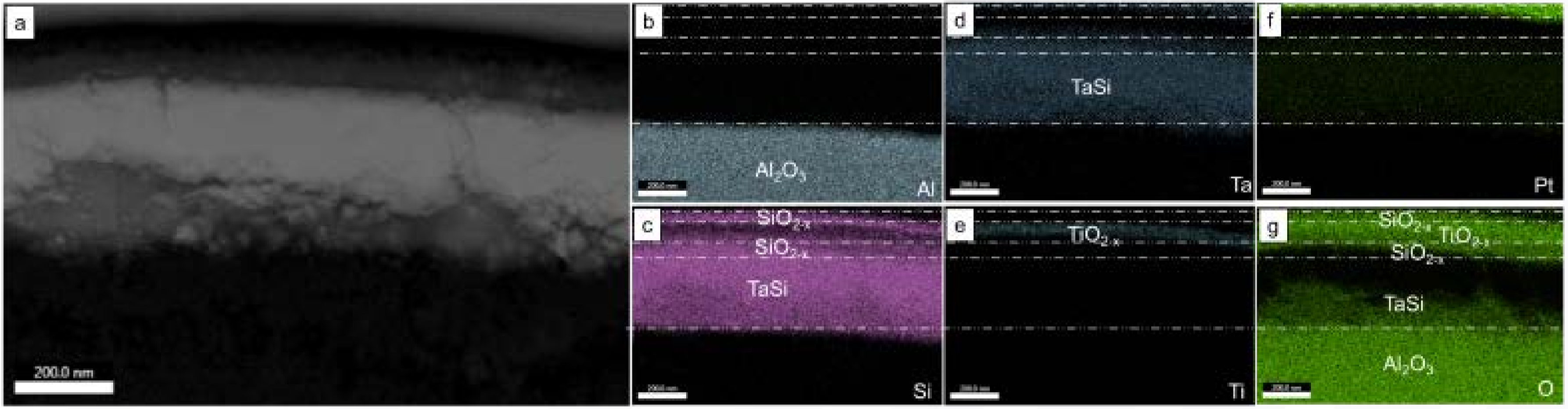
- Diffusion of substrate cations prevents single phase crystallization of $TaSi_2$
  - o Ni compounds formed instead
- 1 µm barrier layer of Al_2O_3 allows for $TaSi_2$ crystallization
- Optical performance with barrier layers matches stack performance on Si



Changes in Tantalum Silicide After Exposure (300 h)

- $TaSi_2$ is stable < 500 °C in air
- Material changes observed at higher temperatures, resulting in decreased α, η
- $TaSi_2$ base layer appears to be oxidizing





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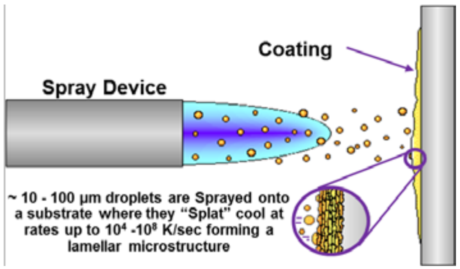
Thermal Spray Coatings & Laser-Treatment

Laser-treatment of a thermal spray coating is a practical pathway for manufacturing a highly efficient, ceramic surface on a CSP receiver.



Spray coated boiler tubes
www.asbindustries.com

Thermal Spray:

- Commercially available equipment & materials
- Low cost application, suitable for large components
- Proven technology in high temperature, high thermal cycle applications (gas turbines)

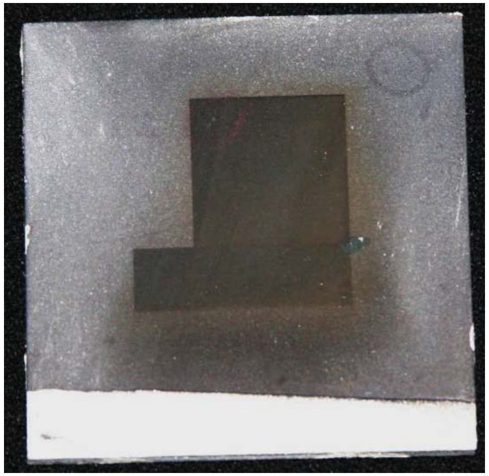
Laser-treatment:

- Raster laser beam over coating surface
- Surface ablation not melting
- Portable, straightforward process
- Largely independent of thermal spray process
- Potential to "refresh" a coating in-situ

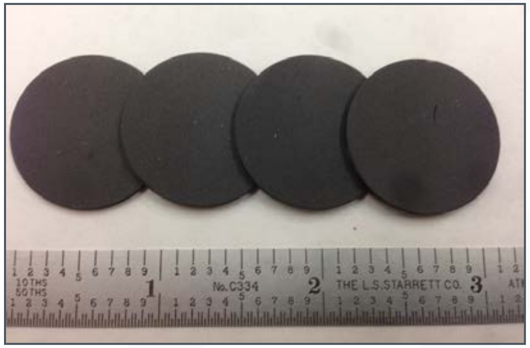
On site Coating of a coal boiler waterwall
www.thefabricator.com

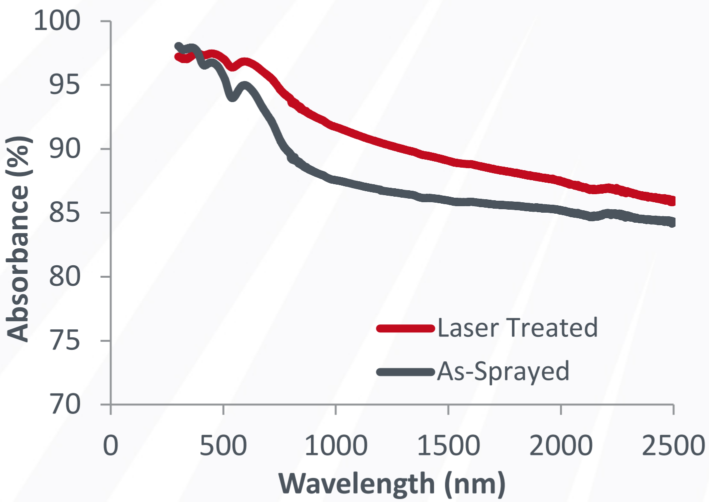
Thermal Spray LSM Perovskite

Novel laser treatment of surface improves optical properties without changing composition or phase of coating (Patent pending)



LSM sample after laser-treatment

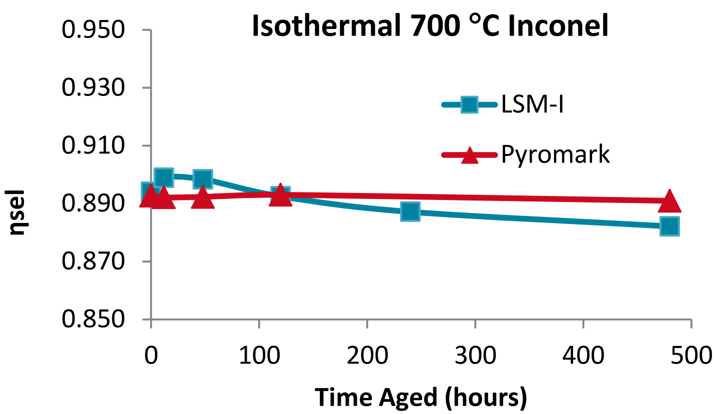


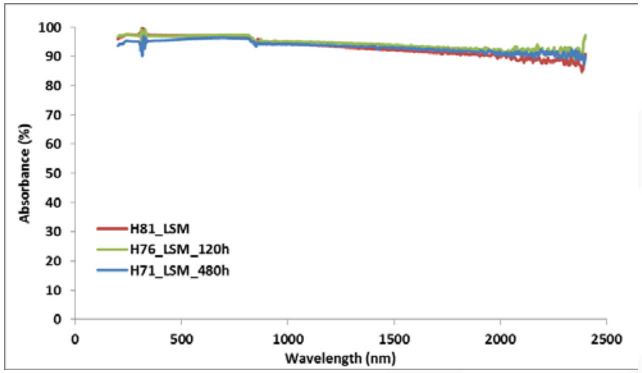


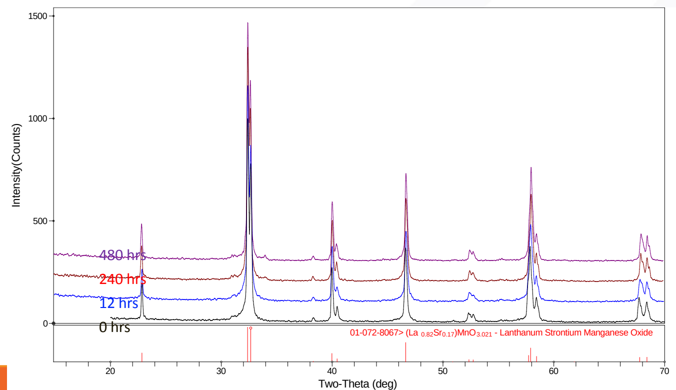
Diffuse reflectance of TS coating before and after laser treatment

Sample	α (sol)	ε (80C rel)	Efficiency, η
LSM #1 As-Sprayed	0.893	0.857	0.821
LSM #1 Laser-Treated	0.958	0.898	0.892

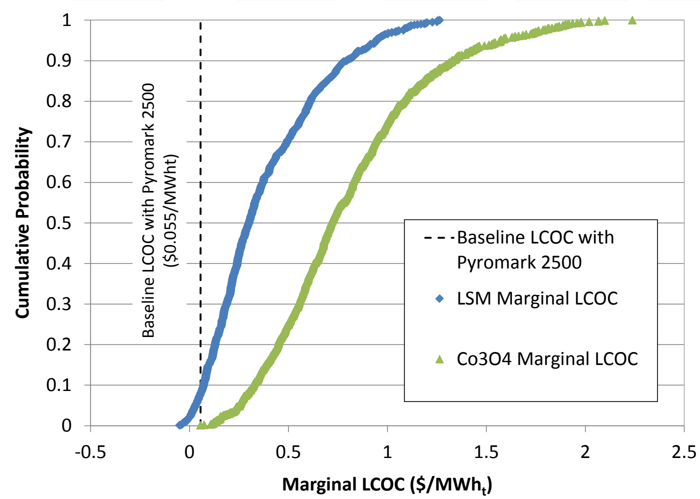
Isothermal Aging (700 °C, 480 h)





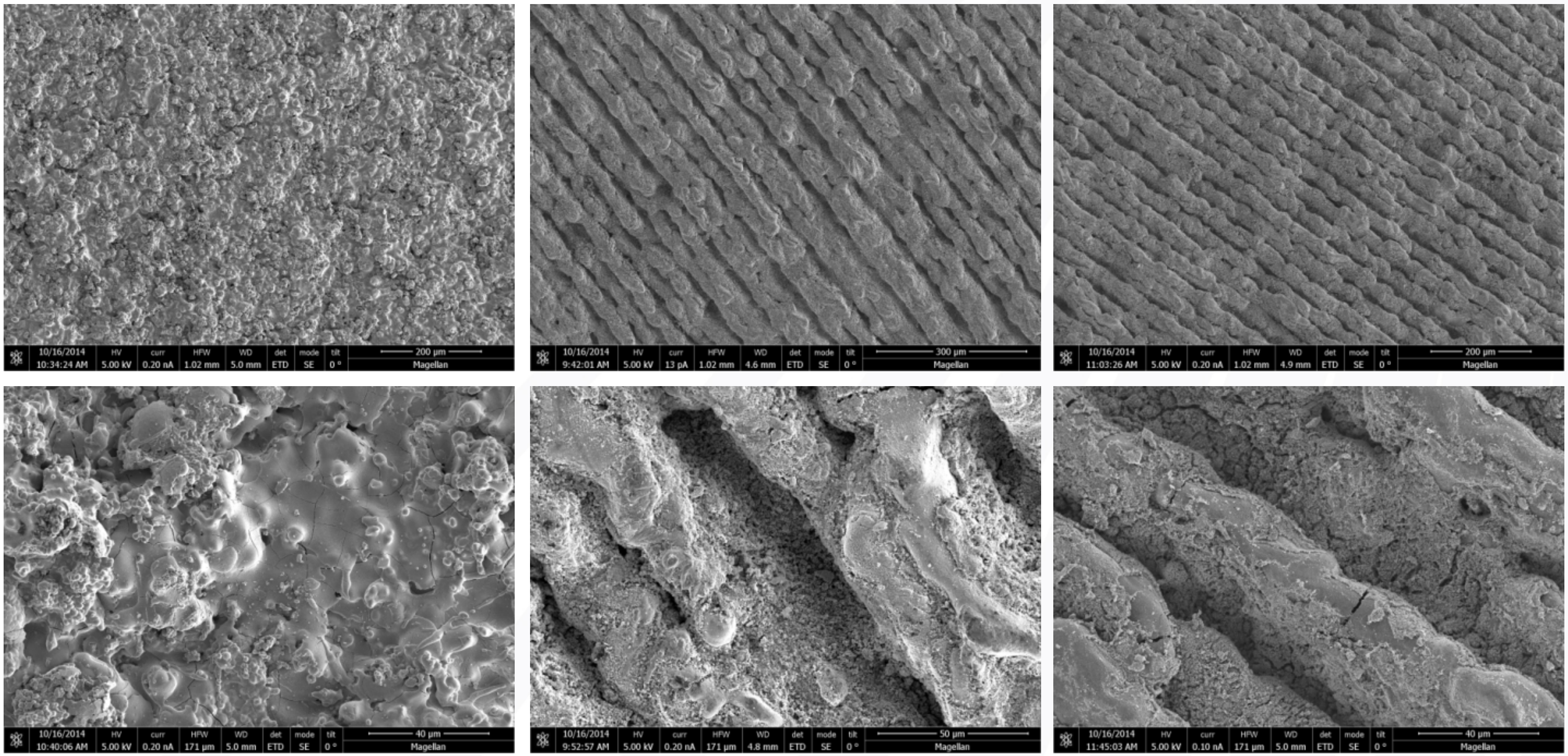


- Slight degradation in optical properties after 700 °C/ 480 h (little to none at 600 °C)
- Little change in XRD or diffuse reflectance upon aging
- With the current (estimated) cost assumptions and performance data, there is a ~10% chance that LSM will yield a marginal LCOC less than the baseline LCOC of Pyromark 2500



LSM Surface Morphology

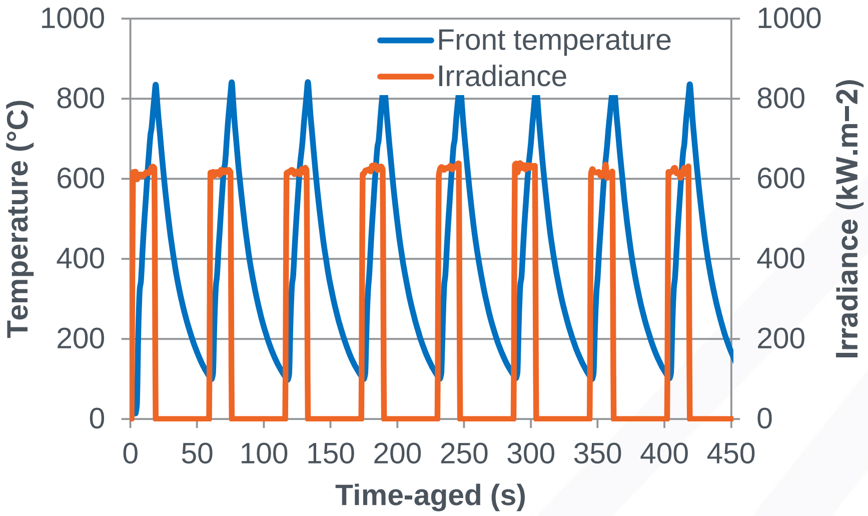
Laser-treated coatings maintain microstructure after isothermal aging



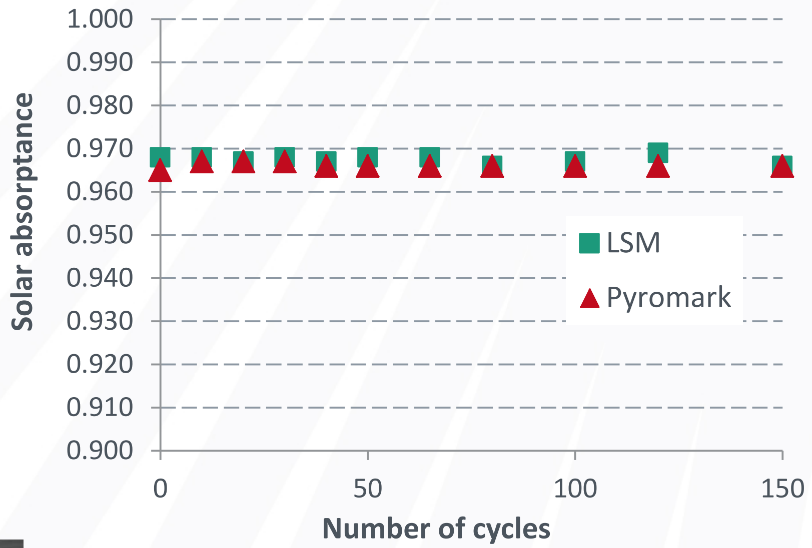
As-Sprayed | Laser Treated | Laser-Treated & Aged 700C/ 480 h

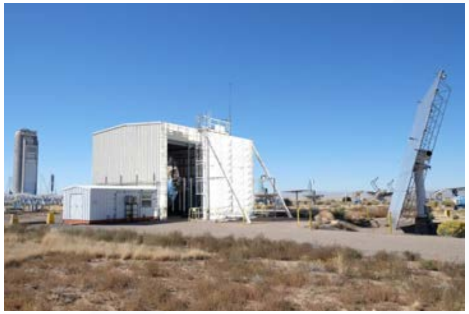
On-sun Testing LSM/Inconel 625

Heating Profile: Automatic controlled forced convective cooling (200 W m^{-2} K^{-1})



600 kW m^{-2} - 0 kW m^{-2} / 700˚C - 100˚C



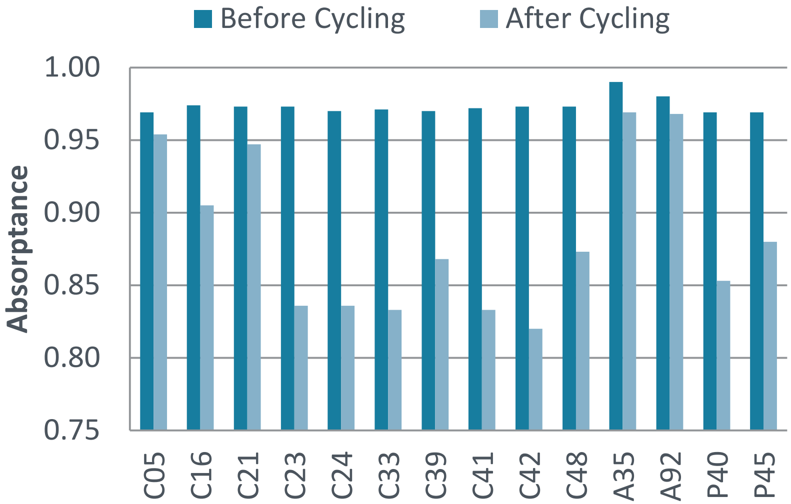


LSM $\eta_{final} = 0.902$

Pyromark $\eta_{final} = 0.893$

Pyromark

- Deposition parameters of Pyromark 2500 were investigated in order to identify factors that contribute most to coating performance
- Design of Experiment executed; many of the coatings delaminated during curing (top right)
- Coatings that survive the curing process generally survive isothermal aging at 700 °C / 96 h with no change in optical properties
- Analyses point toward the following optimized deposition parameters to maximize likelihood of intact coatings with most favorable η:
  - *Grit blasted (rough) substrate surface*
  - *Small paint thickness (25 – 30 μm)*
  - *Slow curing rate (5 ℃/min)*
  - *Curing temperature near 650 ℃*
- However, when exposed to rapid cycling at 600 kW/m^2 / 700 °C on solar simulator, coating properties degrade quickly; results are preliminary and the mechanism of degradation has not yet been determined (bottom right)



Summary

NREL

- $TaSi_2$-based multilayer stack shows promise for SSA applications
- Stack efficiency as designed exceeds that of Pyromark
- Stack Design is air stable to T <500 °C
- 1 µm Al_2O_3 barrier mitigates substrate interference of $TaSi_2$ crystallization
- Material changes of base layer observed at T>600 °C in air
- High flux solar furnace stage developed for measurement and testing of on-sun receiver material efficiency

SNL

- Thermal-sprayed LSM that was surface modified using a laser treatment shows improved absorptivity
- Coatings show no sign of degradation and little, if any, degradation in absorptance after Isothermally aging at 600 and 700 °C/480 h
- Preliminary on-sun tests at 700 °C also show good performance vs. Pyromark
- High emissivity of the coatings remains a challenge

Path to Market

- Protecting the financial investments of potential commercial partners is considered critical, hence IP protection through the patent process is a priority. Filings to date include:
  - Aaron C. Hall and David P. Adams, "High Durability Solar Absorptive Coating and Methods for Making Same." Filed 26-Feb-15, Appl. #14/632,838 (SNL)
  - C. E. Kennedy "High Temperature Solar Selective Coatings," Patent # 8893711, Awarded 11/25/2014. (NREL)
- Partner with key players through CRADA and FOAs (e.g. SBV, TCF) to maximize deployment opportunity
- Develop techno-economic analysis to accurately determine the effect of integrating new SSA coatings into a CSP plant
- Encourage stakeholders to utilize LCOC tool to evaluate costs of various SSA coatings throughout industry using a common metric

Thank You