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Thermal Sprayed Oxide Coatings for Concentrating Solar Power Receivers

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Sandia National Laboratories

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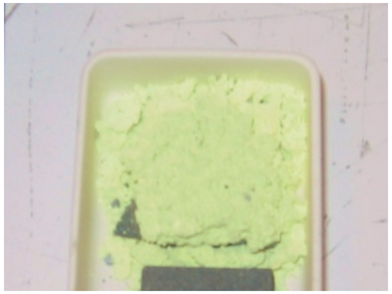
Motivation

- 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 (α > 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


Credit: eSolar



Goals

Improved selective absorber coating 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

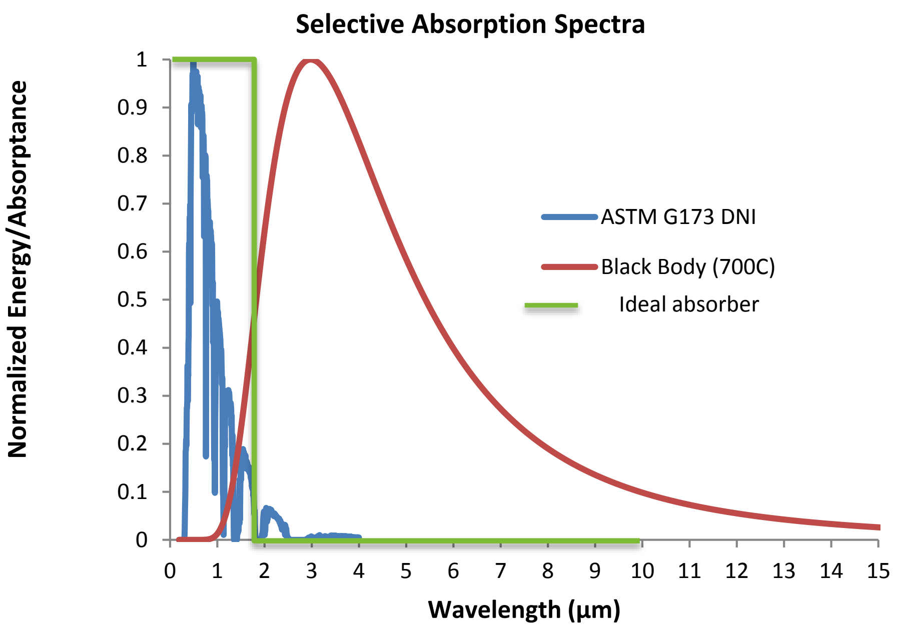
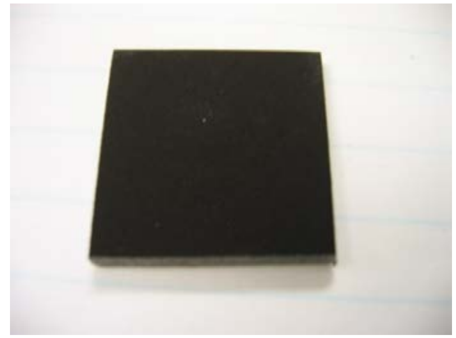


Figure of Merit, η_{sel}

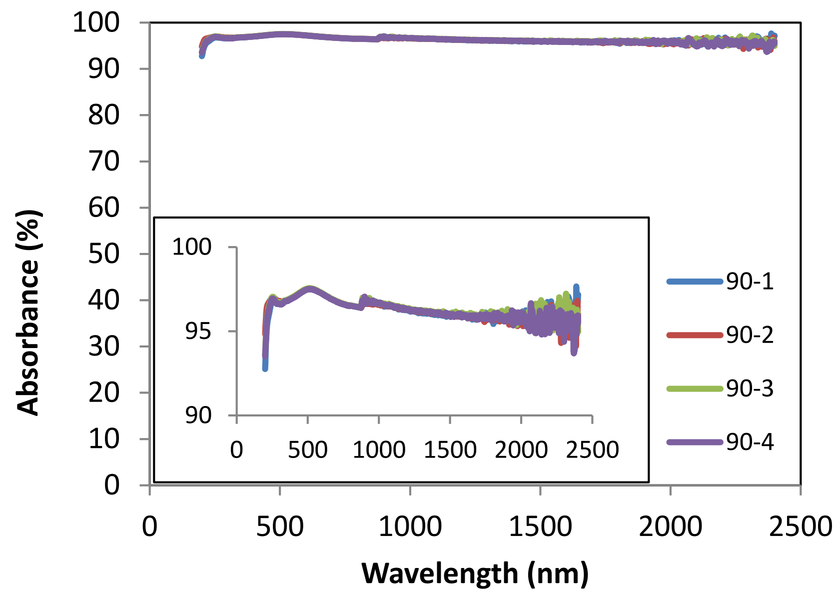
$$\eta_{sel} = \frac{\alpha_s Q - \varepsilon \sigma T^4}{Q}$$

- α_s = solar absorptance
- Q = irradiance on the receiver (W/m^2)
- ε = thermal emittance
- σ = Stefan-Boltzmann constant (5.67×10^{-8} $W/m^2/K^4$)
- T = surface temperature (K)

Pyromark 2500



Sample	α	ε	FOM
1	0.965	0.861	0.889
2	0.966	0.874	0.890
3	0.965	0.865	0.889
4	0.965	0.841	0.890



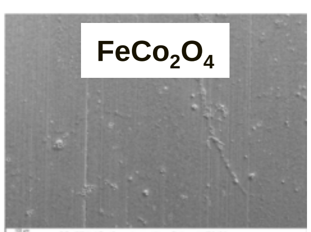
Materials Development

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

Spin Coating

Facile synthesis of coatings with varying formulations and dopant concentrations

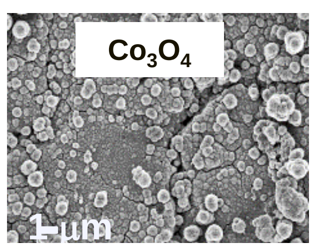
Allows for rapid deposition and optical screening of a composition space



Electrodeposition

Novel approach to screening solar selective materials

Can result in unusual surface morphologies

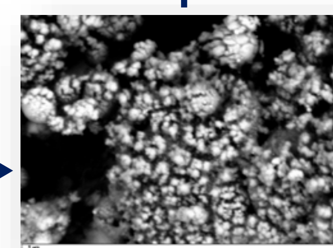


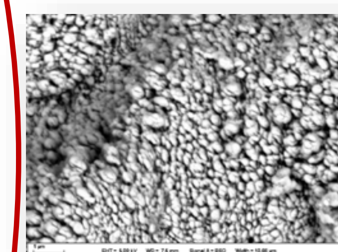
Thermal Spray

High-surface area coating technique

Ability to coat in the field

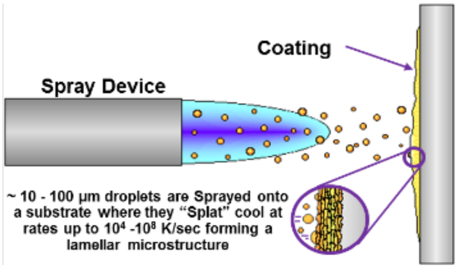
Can modify surface morphology in an efficient and cost-effective manner





Thermal Spray Coatings

Cr_2O_3 and LSM are extremely stable ceramic materials with proven success in high temperature coating applications



Thermal Spray

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

Chrome Oxide (Cr_2O_3) and Lanthanum Strontium Manganite (LSM)

- Commercially available, low cost, feed stocks
- Proven application process for large, non-flat surfaces
- History of Cr_2O_3 and LSM coatings in high temperature applications

Chrome Oxide (Cr_2O_3)

- *Melts at 2435° C (4415° F)*
- *Boils at 4000° C (7232° F)*
- *Extreme thermal & chemical stability*
- *Extreme hardness & wear resistance*
- *Insoluble in water, acids, & alkalis*
- *Used for pump and impeller housings*
- *Coatings recommended for service temperatures up to 815° C*

Lanthanum Strontium Manganite (LSM)

- *Family of Pervoskite Materials*
- *Typically melt at temps > 1000° C*
- *Insoluble in water, acids, & alkalis*
- *Used for solid oxide fuel cell electrolytes*
- *Coatings recommended for use up to 800° C*

Thermal Spray Examples

"extreme portability of the equipment allowed spraying operations to be carried out from a cherry picker with the flare boom stood upright, the top section of the flare tower being more than 25m above the ground."

Bluewater Energy Floating Production & Storage Vessel

1,100m^2 of TSA coating applied in 3 weeks for a petrochemical refinery expansion project in Singapore. Coated vessel is 75 meters tall

MTM Metalizing LTD.

Laser-Treatment

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

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

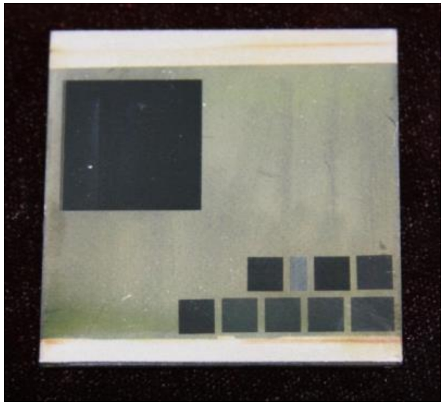
Approach

- Improve coating figure of merit through surface roughening
  - –Literature shows roughening can create "superblack" surfaces
  - –Laser Surface Treatment shown to roughen Si and Ti
    - Femtosecond laser readily accessible at SNL
    - Previous experience changing colors of metal oxides using femtosecond laser-treatment
- Understand why high figures of merit were realized on both laser-treated Cr_2O_3 and LSM surfaces
  - –Microstructural analysis using XRD, SEM, EDS, FIB, & STEM

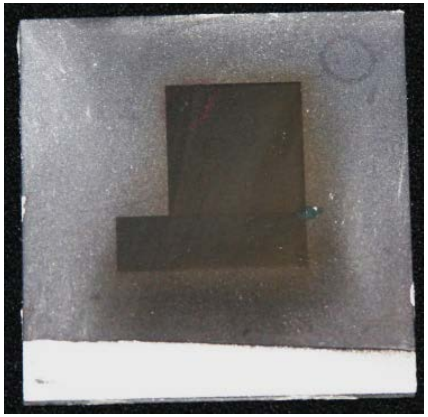
Femtosecond Laser Treatment

Sample	α	ε	FOM
Cr_2O_3 #1 As-Sprayed	0.902	0.866	0.829
LSM #1 As-Sprayed	0.893	0.857	0.821
Cr_2O_3 #1 Laser-Treated	0.959	0.854	0.885
Cr_2O_3 #2 Laser-Treated	0.941	0.743	0.875
Cr_2O_3 #3 Laser-Treated	0.954	0.733	0.886
Cr_2O_3 #4 Laser-Treated	0.948	0.759	0.879
LSM #1 Laser-Treated	0.958	0.898	0.892

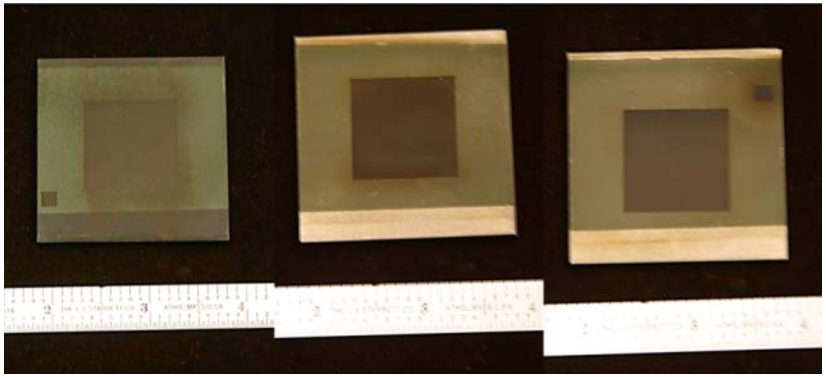
- 800 nm Spectra-Physics® laser capable of 100 Femtosecond pulsed output at 1khz frequency
- Laser-treatment conducted in an evacuated chamber at pressures ranging from 500 mTorr – 6 Torr



Cr_2O_3 sample after laser treatment



LSM sample after laser-treatment

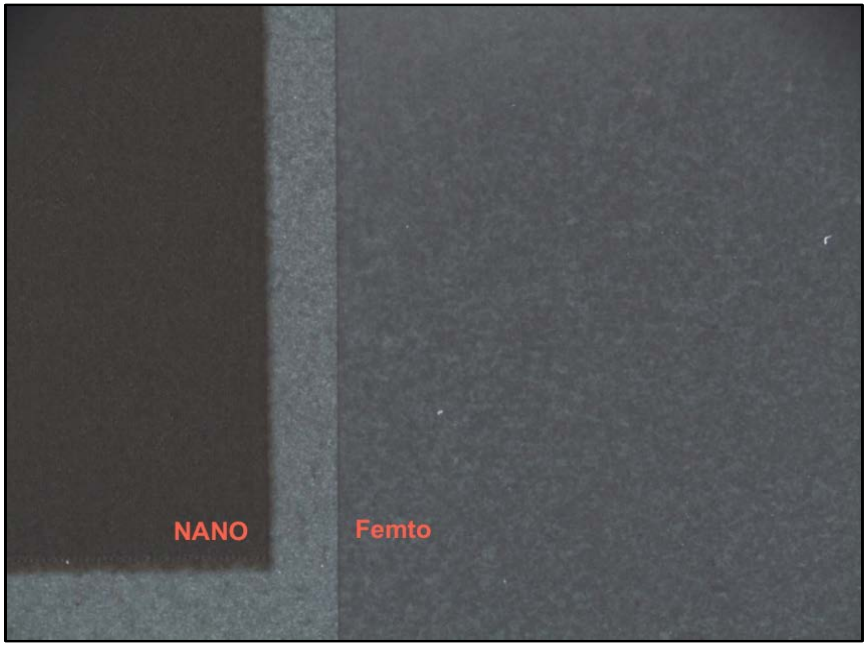


Additional laser-treated Cr_2O_3 samples

Both laser-treated ceramic coatings exhibit a FOM similar to Pyromark®-2500 (FOM = 0.89)

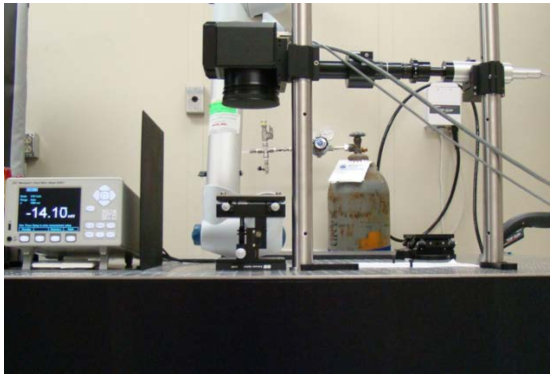
Nanosecond Laser Treatment

- SPI G3 Pulsed Fiber Nanosecond Laser
- Nutfield XLR8 scan head
- Laser Power = 5 W (Commanded)
- Beam Translation Speed = 50 mm/s
- Laser Pulse 50 kHz x 200ns
- Raster Step Size = 40 µm
- Incident beam spot size = 50 µm
- Laser cost ~$25k vs. $500k for femto
- Beam can be split into 4 beams
- Scan speeds up to 500 mm/s possible



Cr_2O_3 sample treated with the Femtosecond laser (right) and the Nanosecond laser (left).

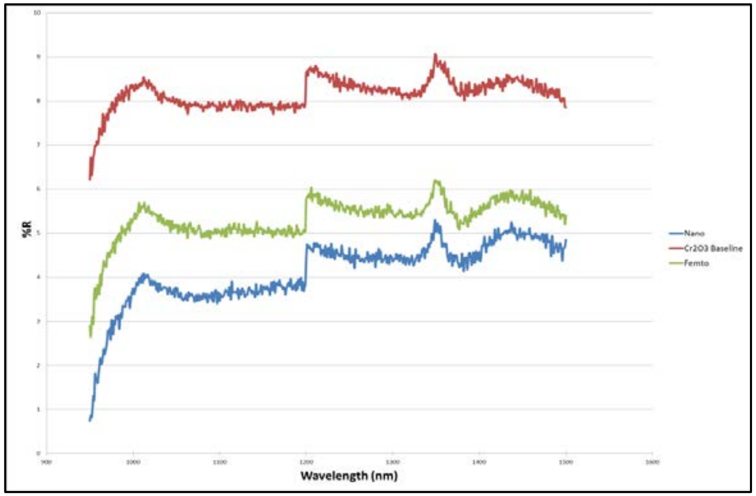
Nanosecond laser and scan head



Nanosecond laser-treatment is 50X faster than femtosecond laser-treatment and potentially 500X faster!

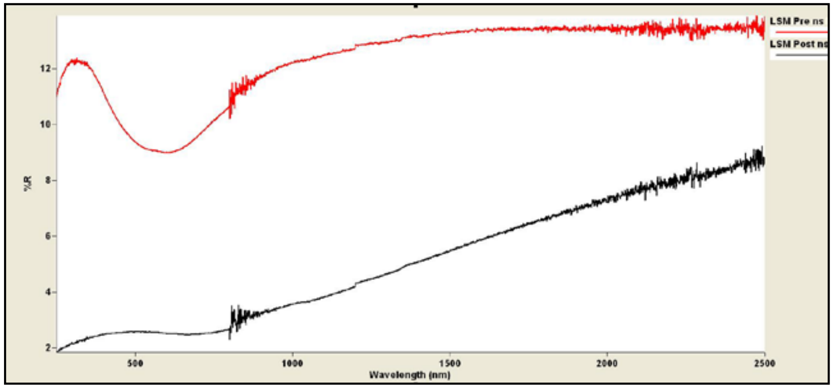
Nanosecond Laser Treatment

Nanosecond laser-treatment significantly reduced the reflectivity of LSM and Cr_2O_3

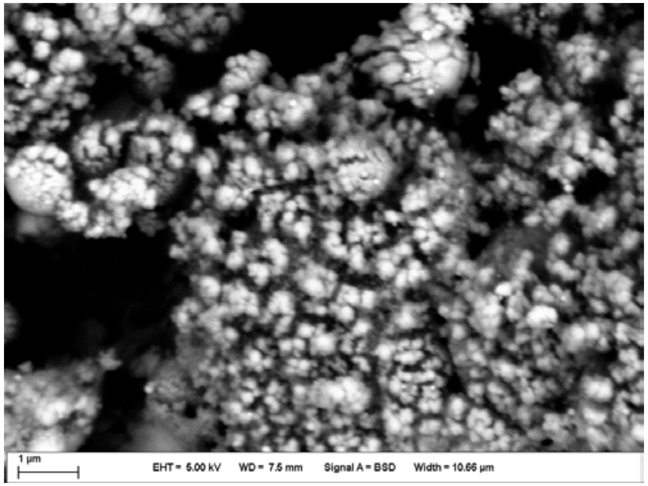


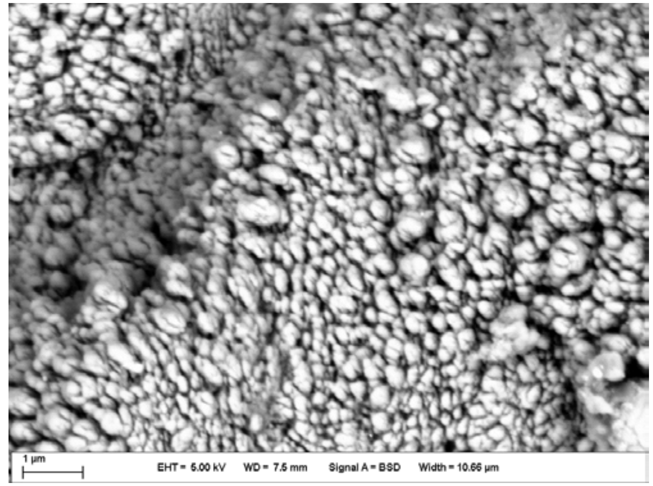
Comparison of as-sprayed Cr_2O_3 (red), Femtosecond laser treated Cr_2O_3 (green), and the Nanosecond laser treated Cr_2O_3 (blue)

Comparison of as-sprayed LSM (red) and Nanosecond laser-treated LSM (black)



Laser Treatment of Cr_2O_3



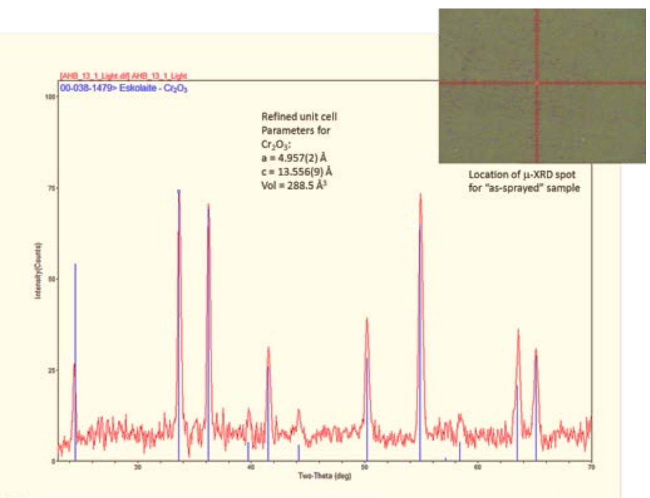


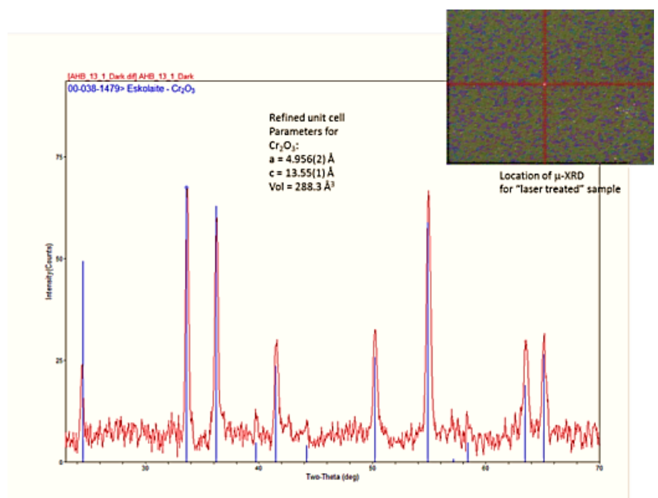
As-sprayed

Laser-treated

SEM Confirms:

- Rough surfaces
- Sub-micron features



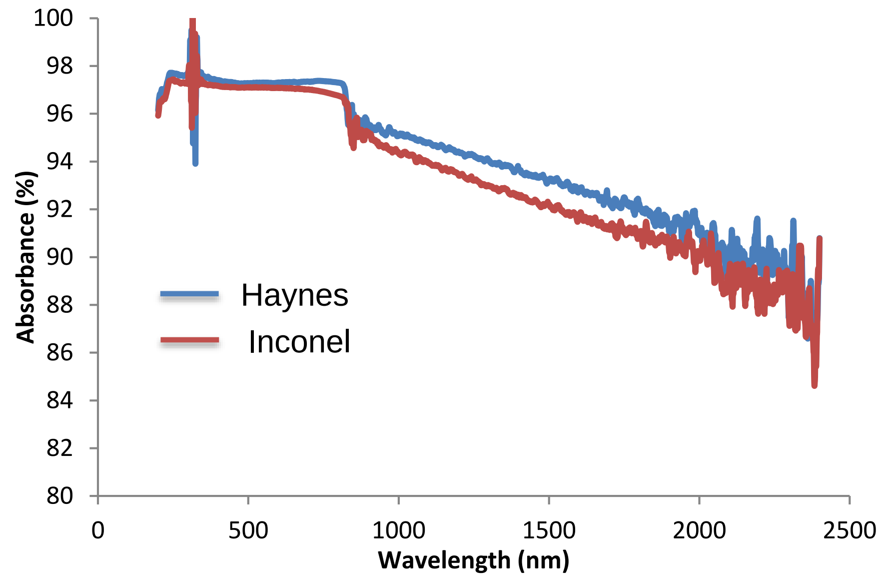


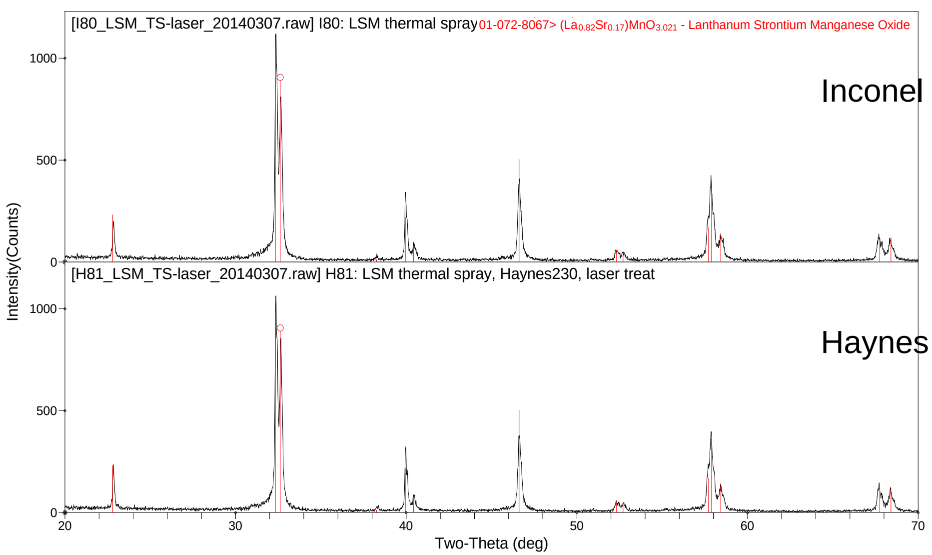
µ-XRD confirms:

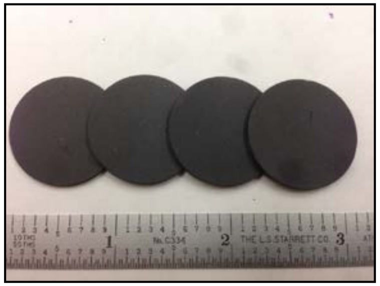
- Cr_2O_3
- Expected lattice parameters
- No gross contamination

Laser Treatment of LSM

No significant difference in intial coating properties between Haynes and Inconel substrate



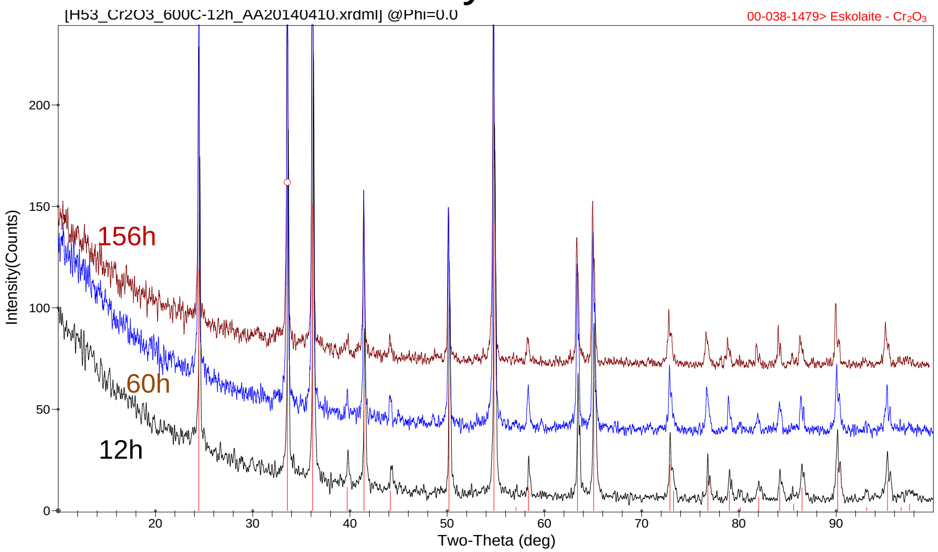




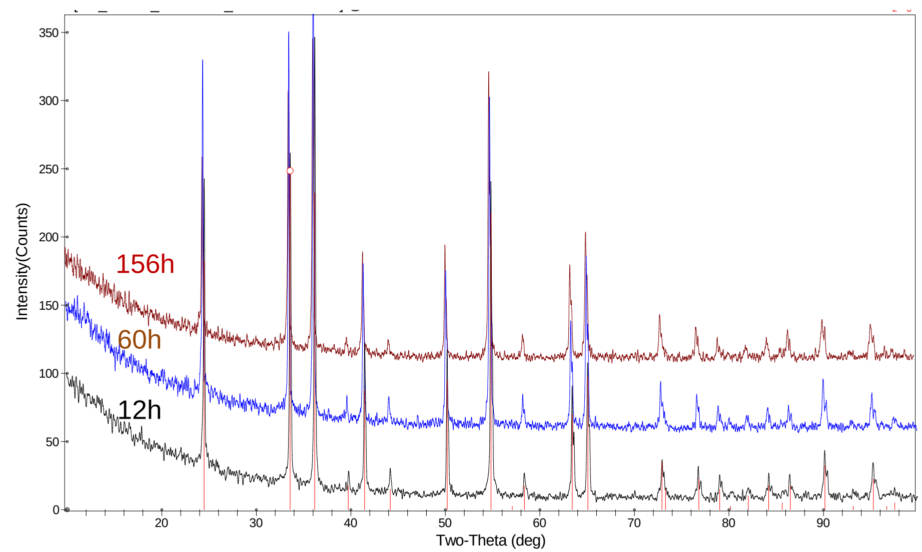
Sample	Substrate	α	ε	η_{sel}
LSM	Haynes	0.955	0.820	0.887
LSM	Inconel	0.971	0.850	0.900

Aging of Cr_2O_3 (600 °C)

Haynes 230



Inconel 625



12 h

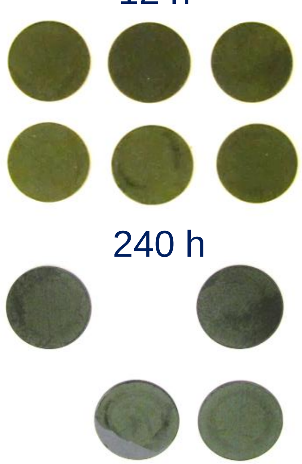
Haynes 230

Inconel 625

240 h

Haynes 230

Inconel 625



- XRD shows Cr_2O_3 phase throughout aging process
- However, optical properties quickly degrade
- Obvious physical degradation of coatings visible, along with color change from black to green

Aging of Laser-Treated LSM (600 °C)

- Solar selectivity remains constant LSM on both substrates
- Coatings remain dark to the eye
- Diffuse reflectance essentially unchanged

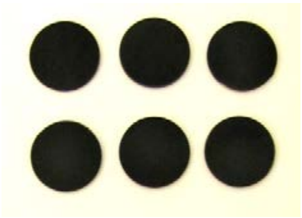
Optical Properties before/after 600 ^oC/240 h

Aging	Substrate	α	ε	η
None	Haynes 230	0.965	0.840	0.895
240 h	Haynes 230	0.969	0.835	0.900
None	Inconel 625	0.963	0.823	0.894
240 h	Inconel 625	0.962	0.811	0.894

12 h

Haynes 230

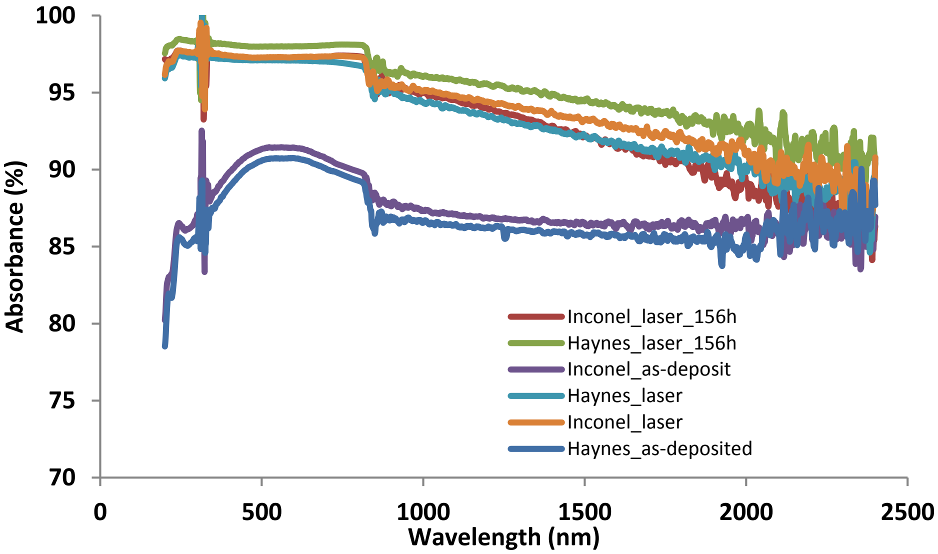
Inconel 625



240 h

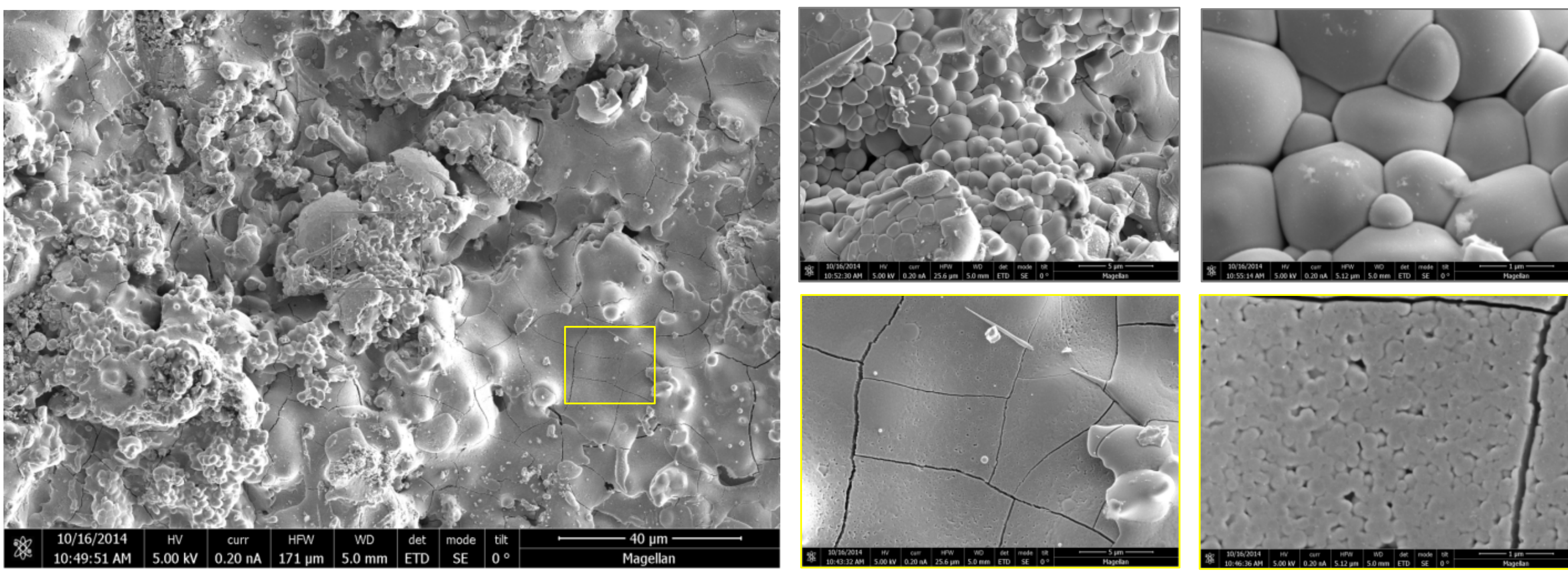
Haynes 230

Inconel 625

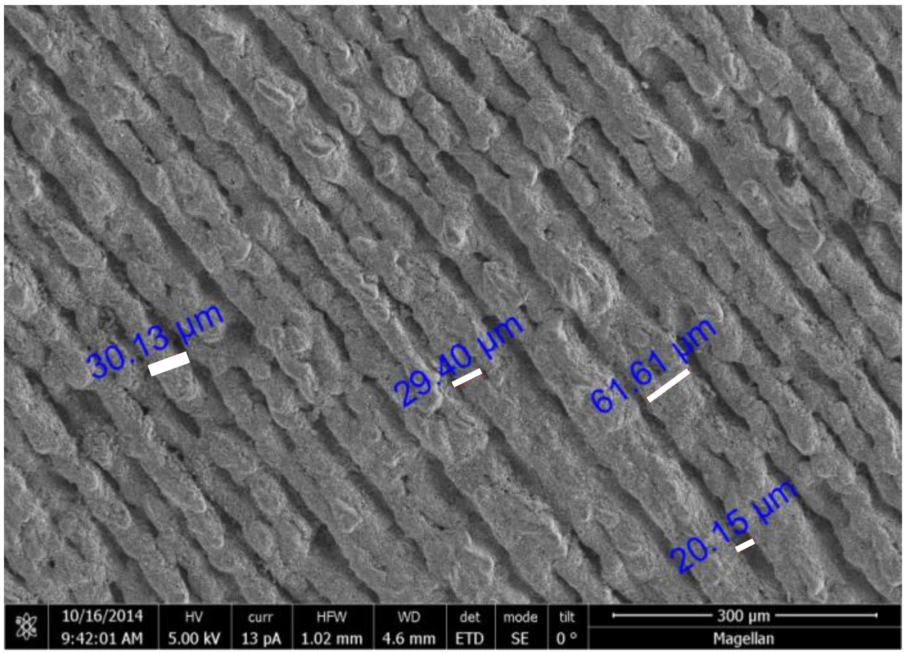


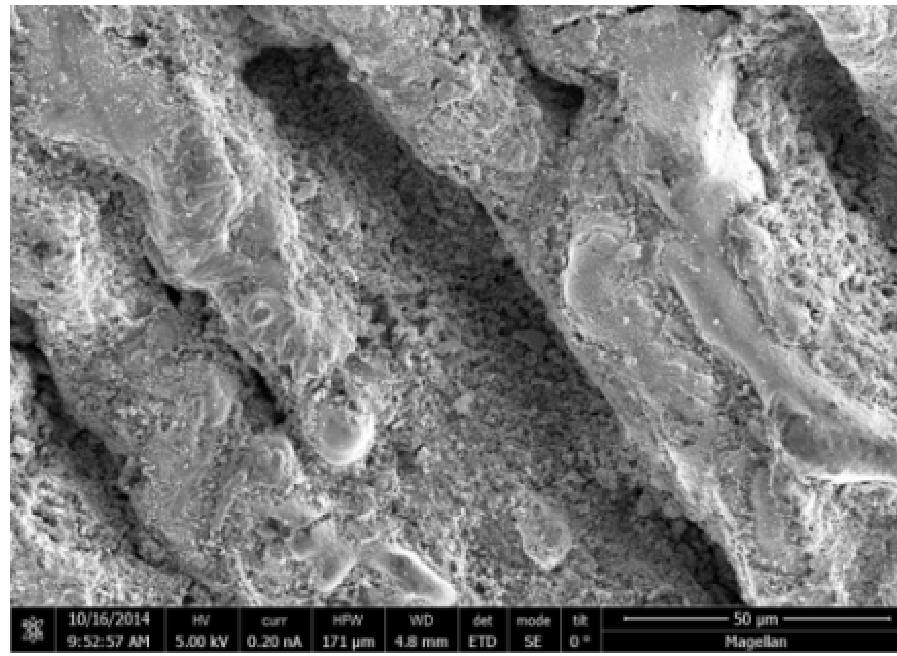
As-Sprayed LSM

- The as-sprayed surface contains solidification structures and micro-cracking typical of a ceramic thermal spray coating
- Surface morphology characteristic of liquid / semi-liquid droplet impact and solidification



SEM of Nano-treated LSM



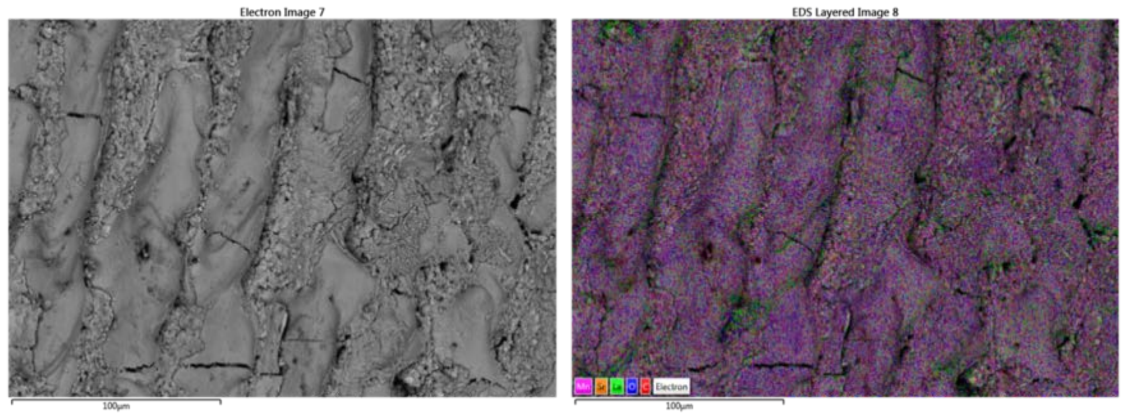


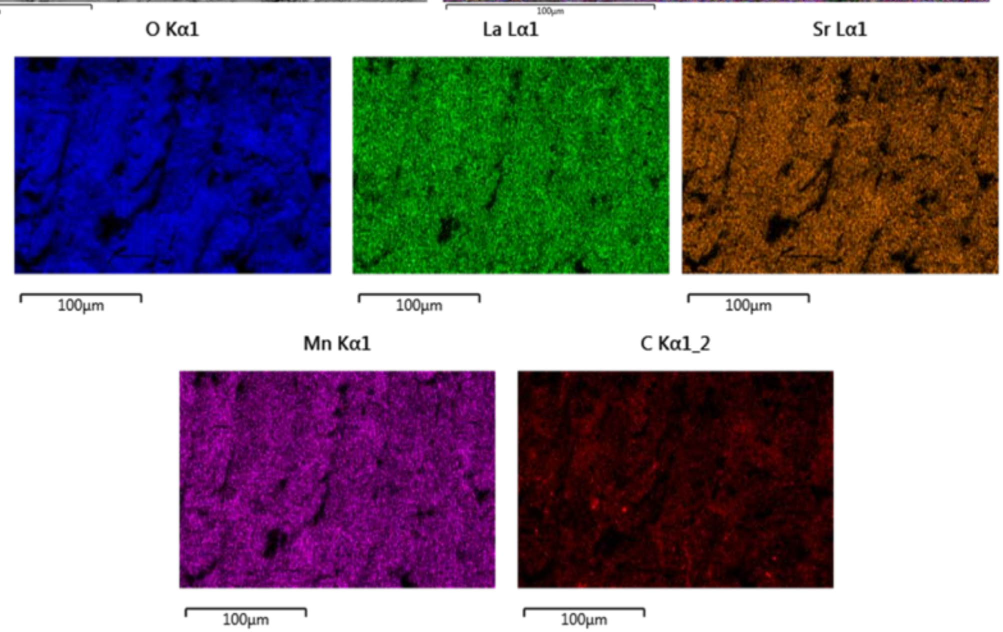
Trenches: ~ 10 μm wide; ~30 μm spacing

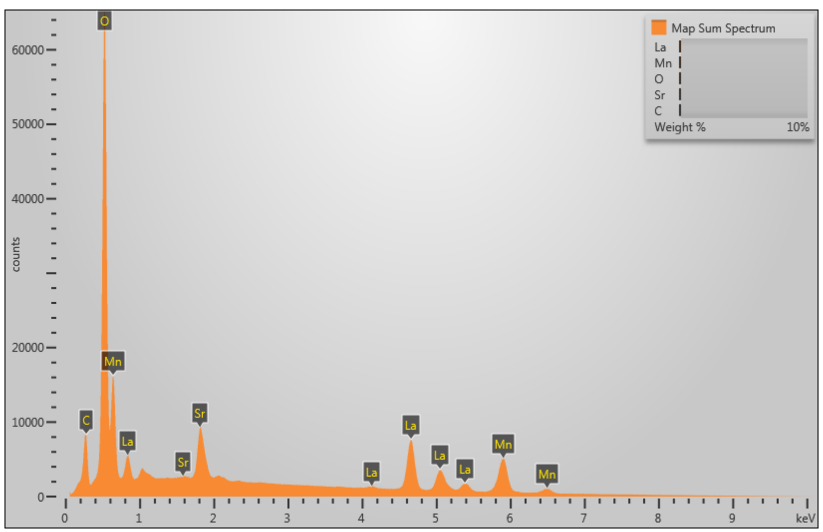
EDS

EDS maps show La, Sr, and Mn on unaged surface

- Chemical mapping does not reveal elemental segregation
- La, Sr, and Mn uniformly distributed

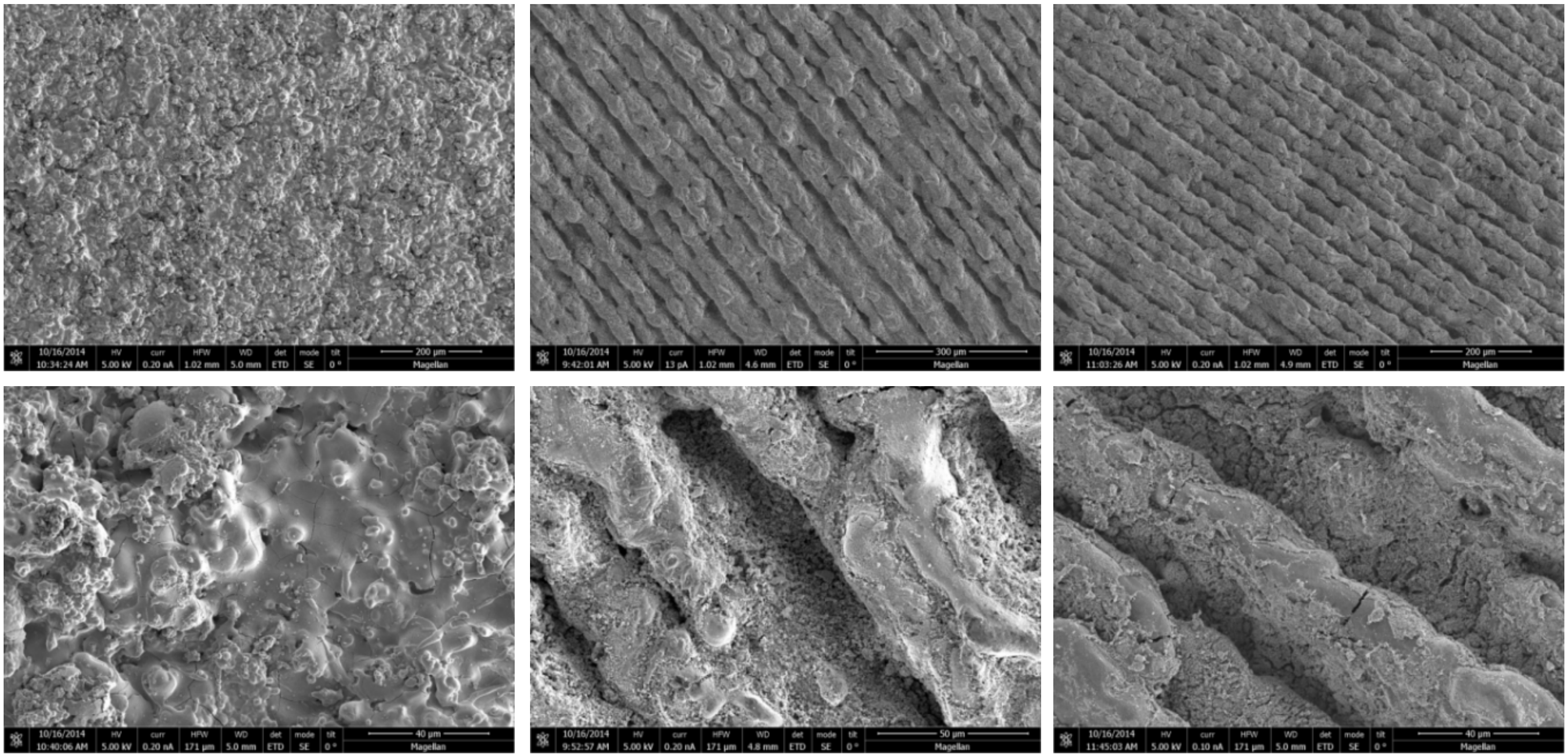






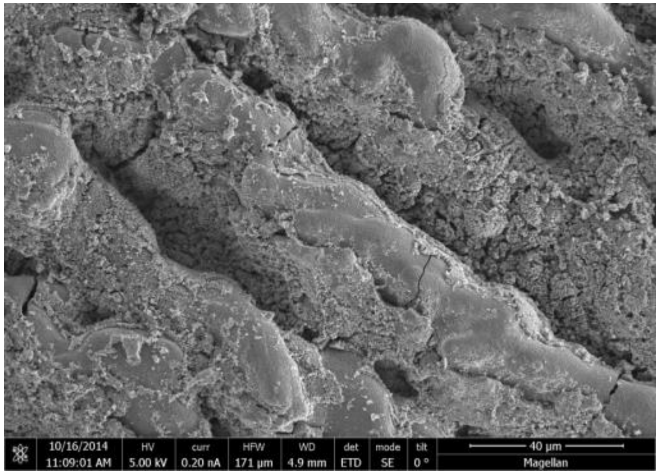
LSM Surface Morphology

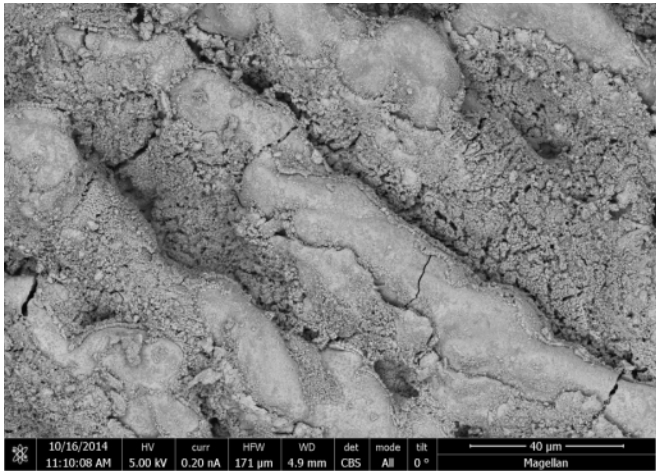
Laser-treated coatings maintain microstructure after isothermal aging



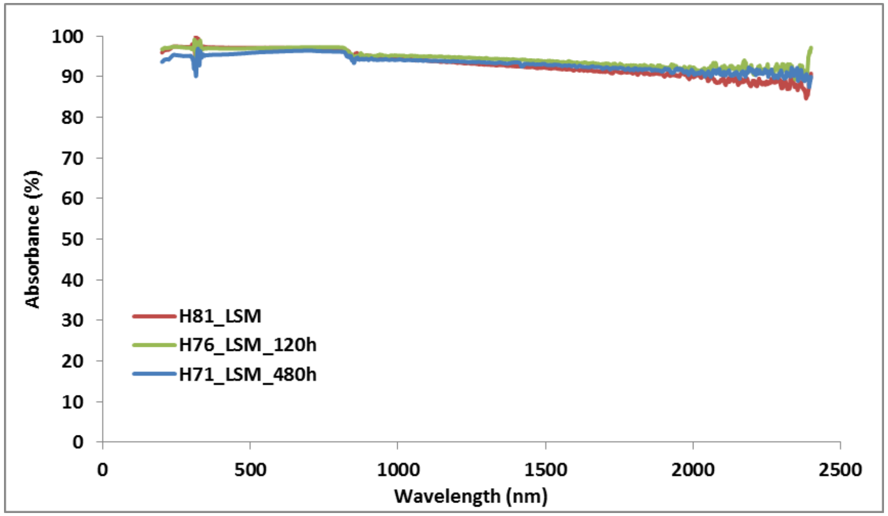
As-Sprayed | Laser Treated | Laser-Treated & Aged 700C/ 480 h

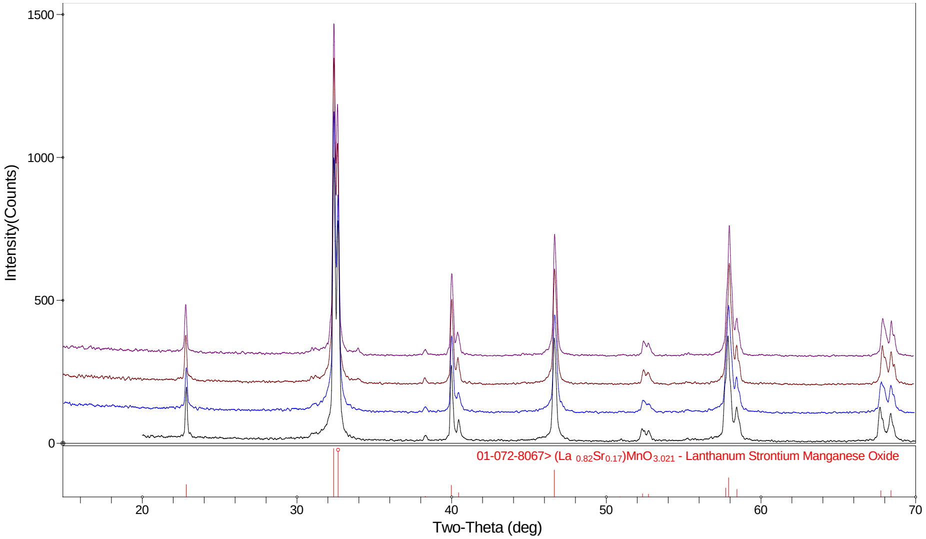
Aged LSM (Haynes, 700 ºC/480 h)



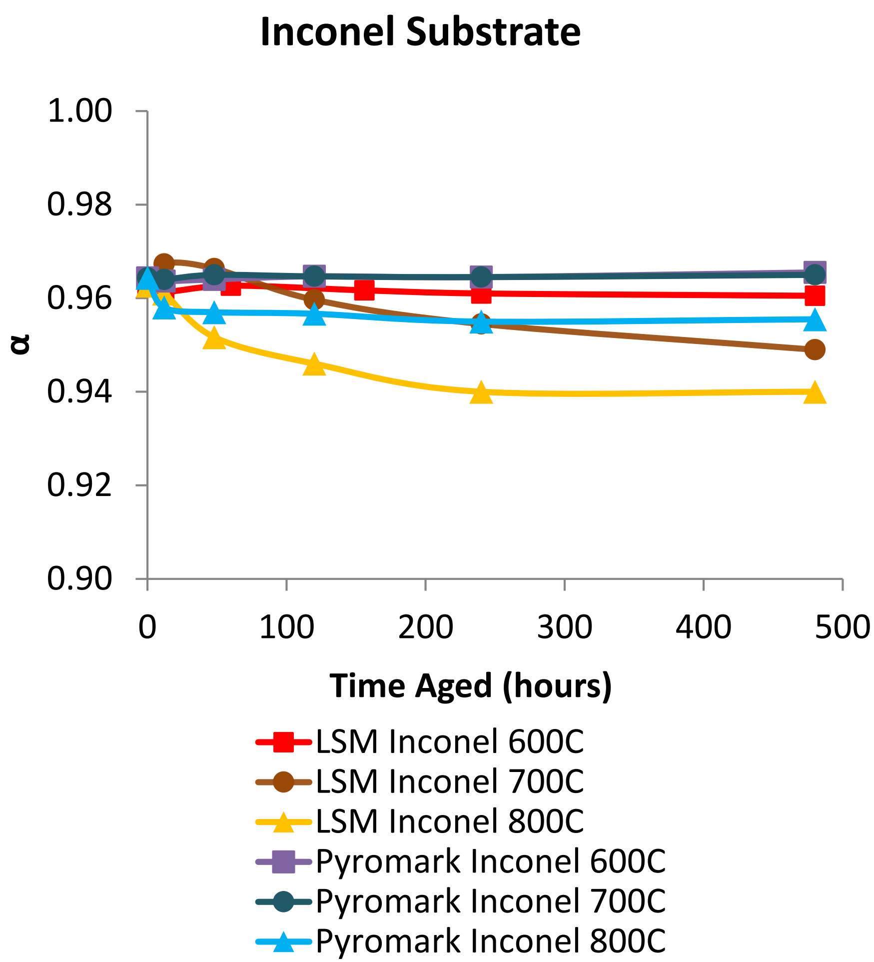


Little change in XRD or diffuse reflectance upon aging





Aging: Absorptance vs. Temperature



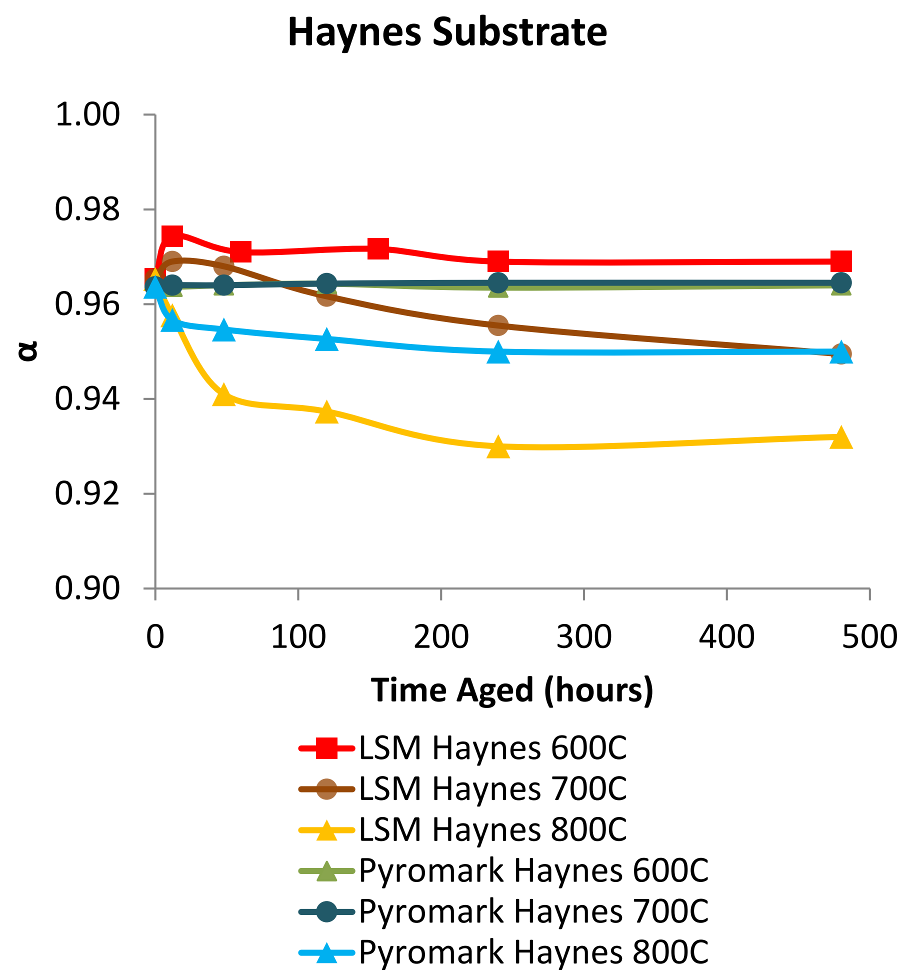
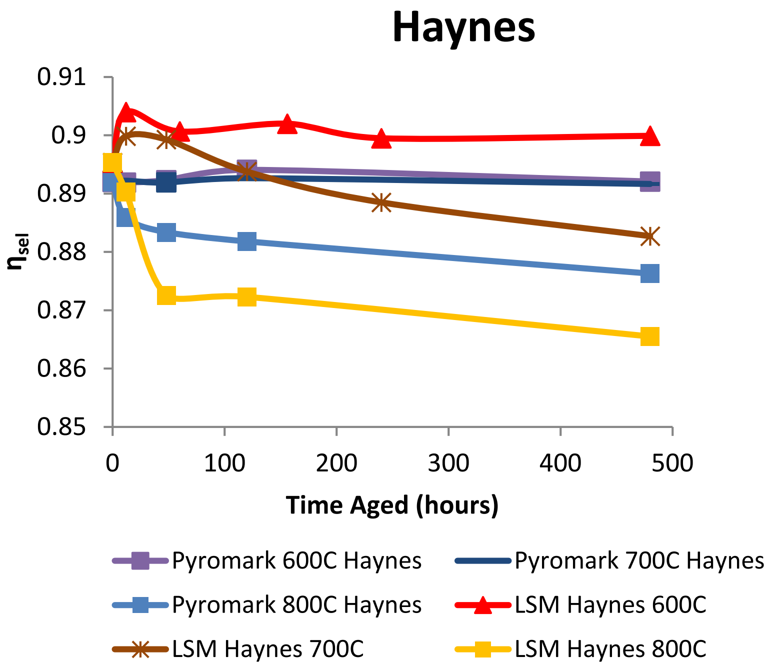
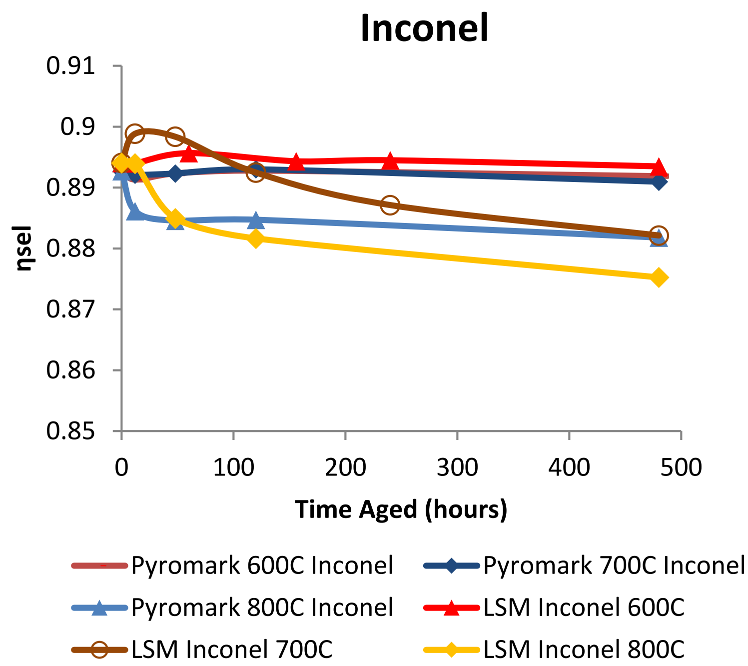
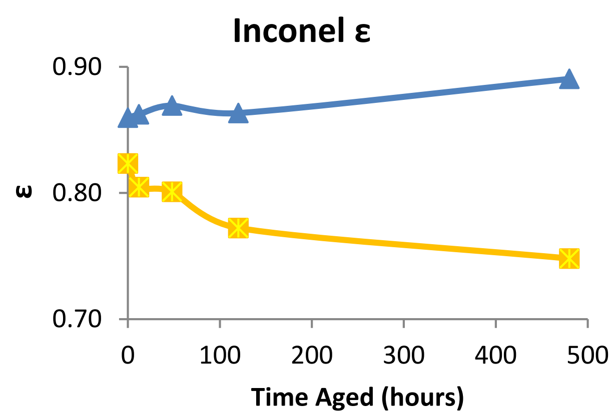


Figure of Merit







- Decrease in η_{sel} of Pyromark at 800 ^{o}C despite good α while that for LSM does not change as dramatically
- Decrease in ε of LSM at 800 ^{o}C; less dramatic at lower T

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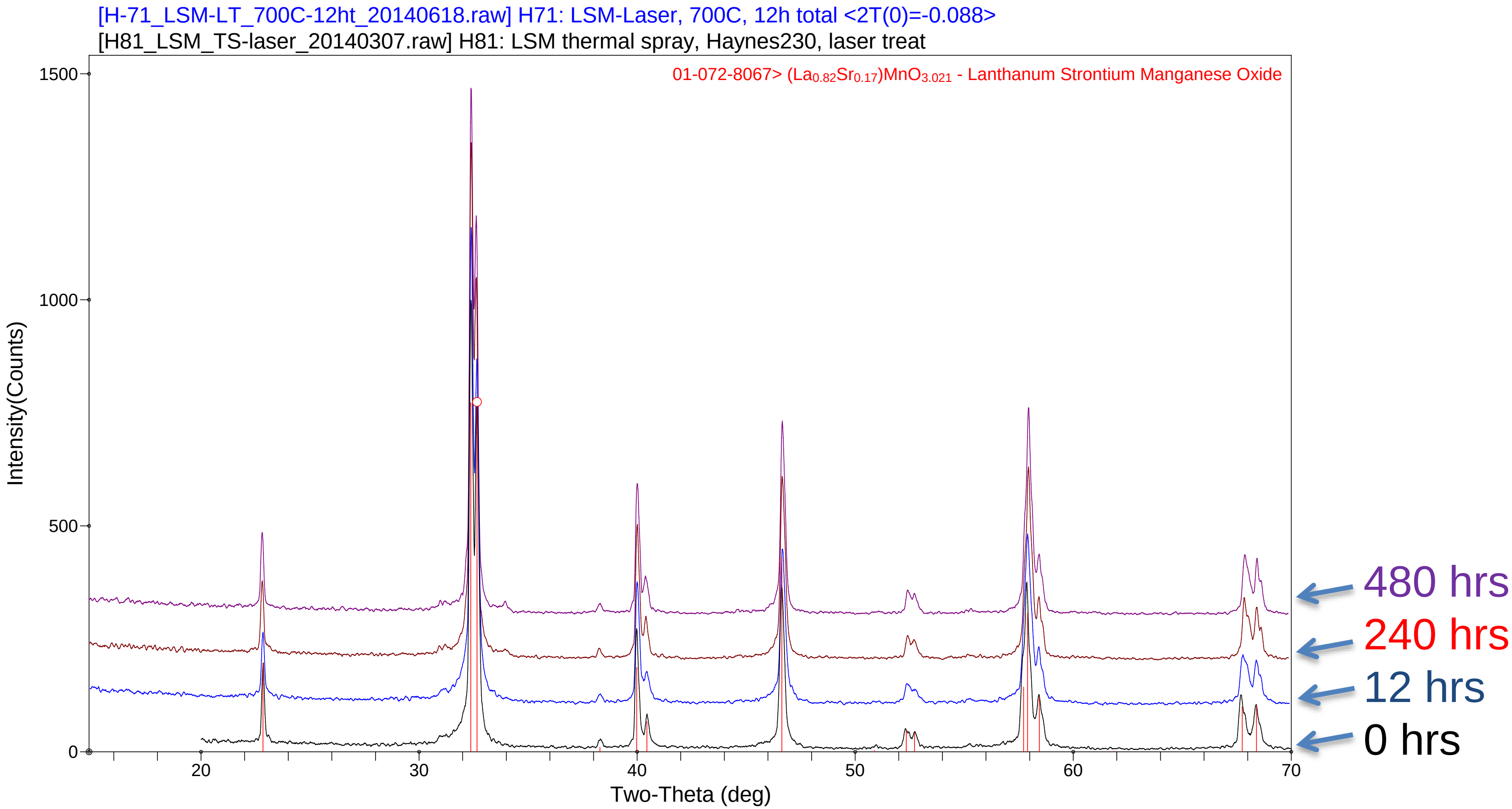
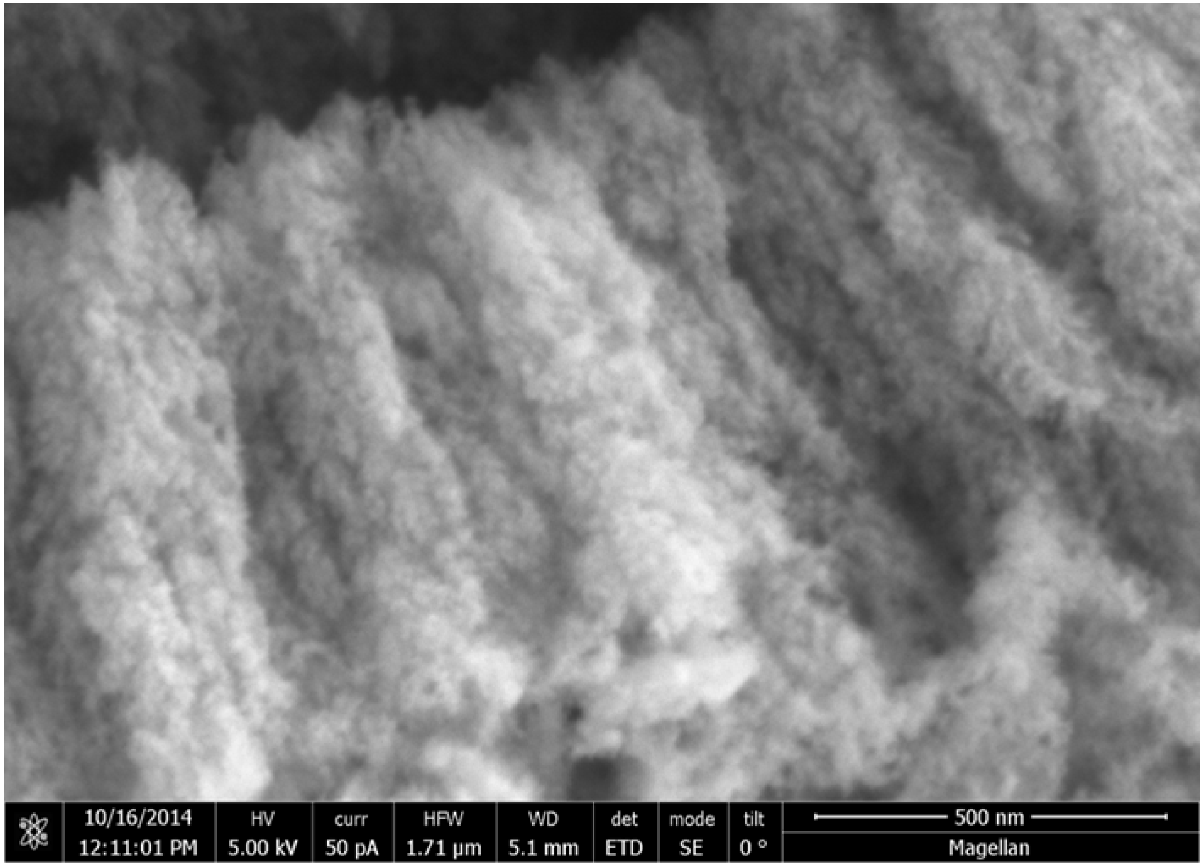
LSM Thermal Aging



XRD shows no phase change upon aging

Re-deposition in Unaged LSM

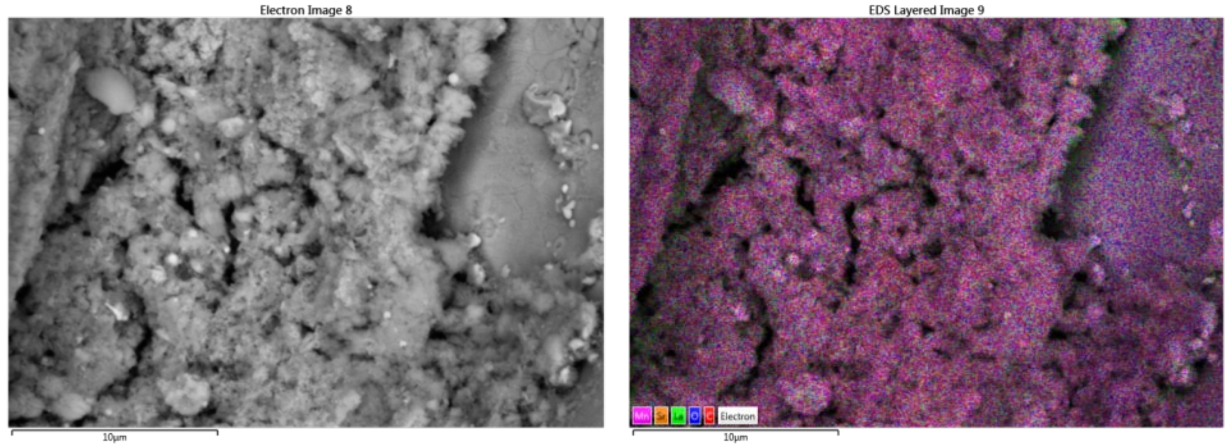


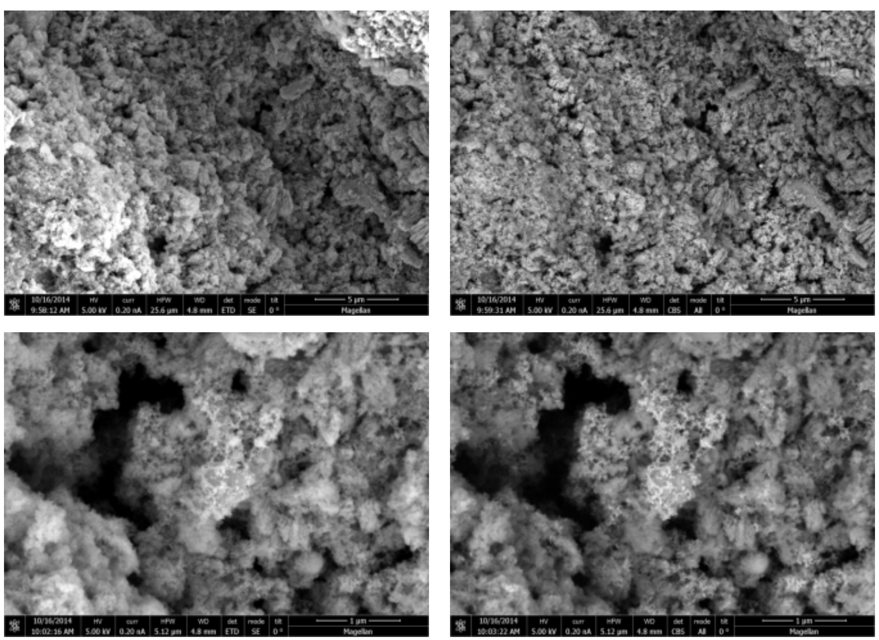
- Columnar structure suggests LSM re-deposition during laser treatment
- Significant nano-scale structure in the re-dep material could trap light
- Re-dep morphology may be controllable with substrate temperature

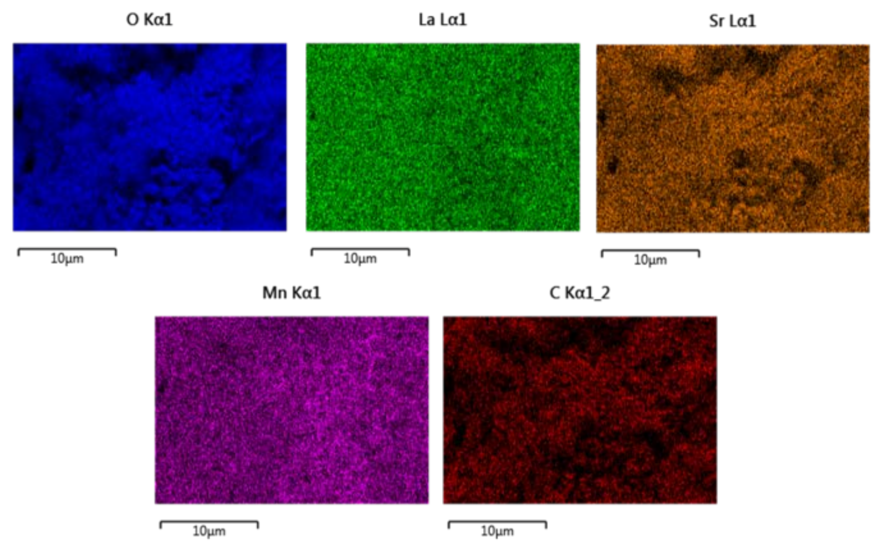
Re-deposited Material (Unaged LSM)

Bottom of trench:

- Lots of nanoscale structure
- Homogenous composition

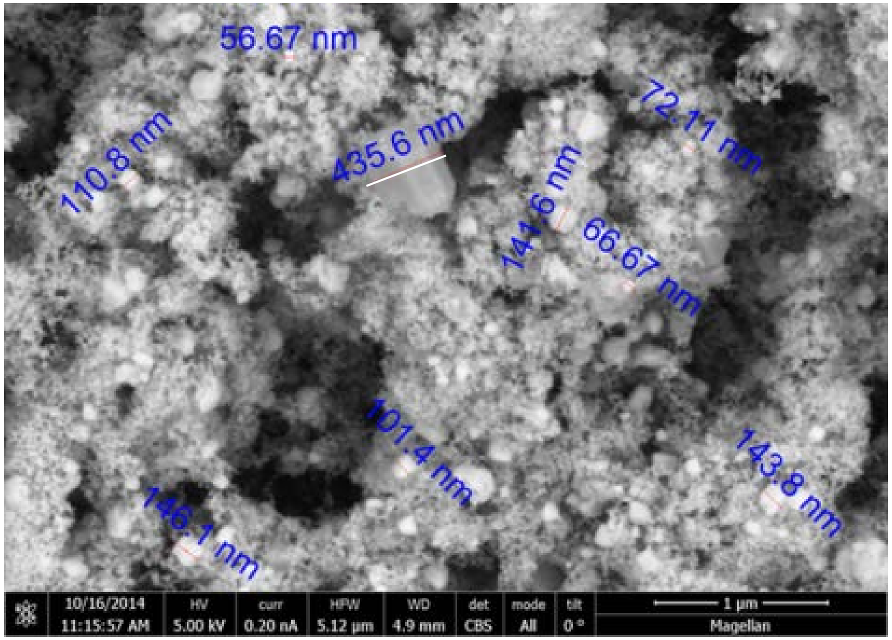


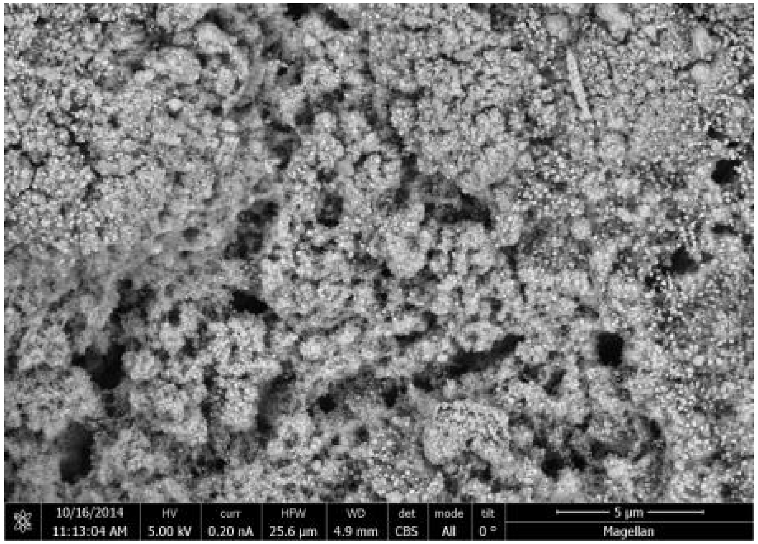


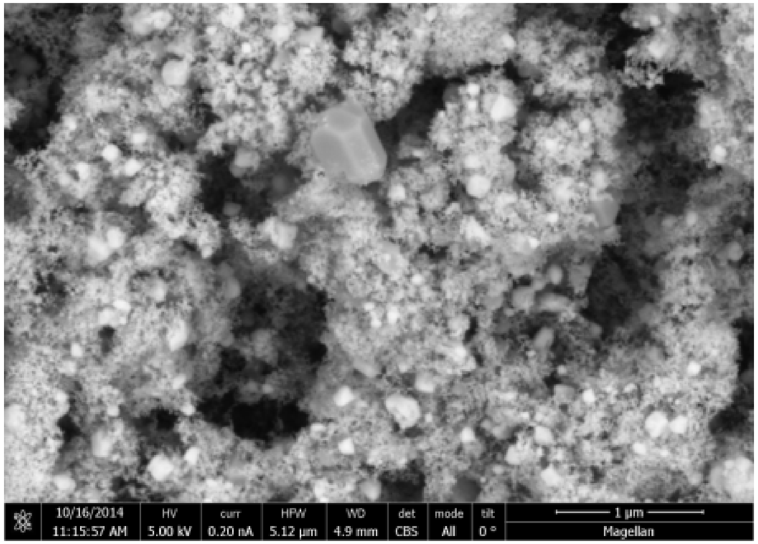


Aged LSM Trench Bottom

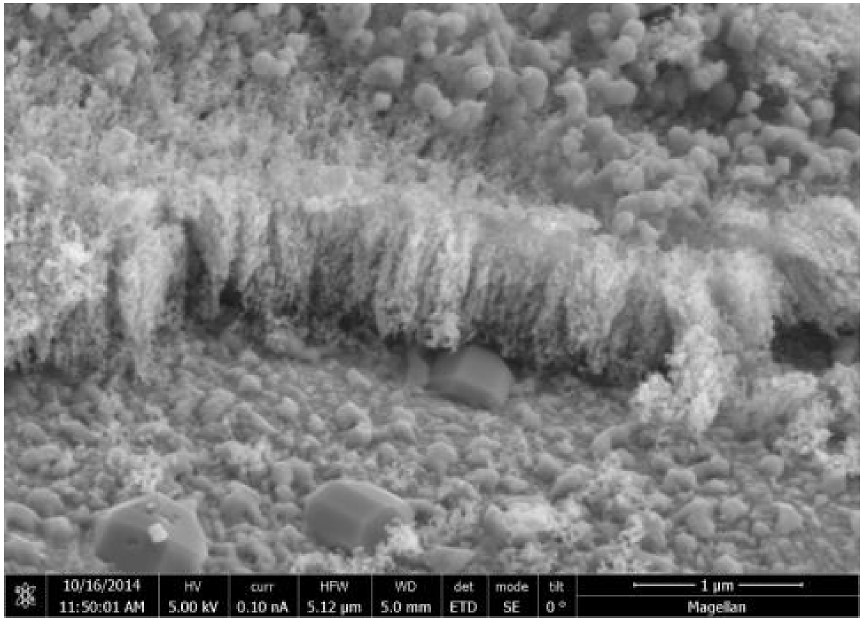
- Nanoscale re-deposition remains
- 50-500nm crystallites visible in re-dep material

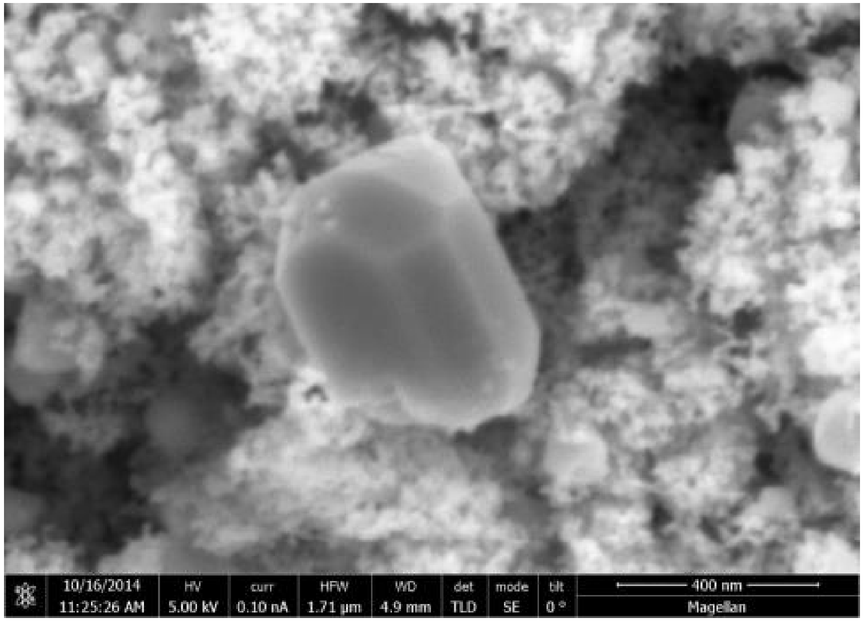






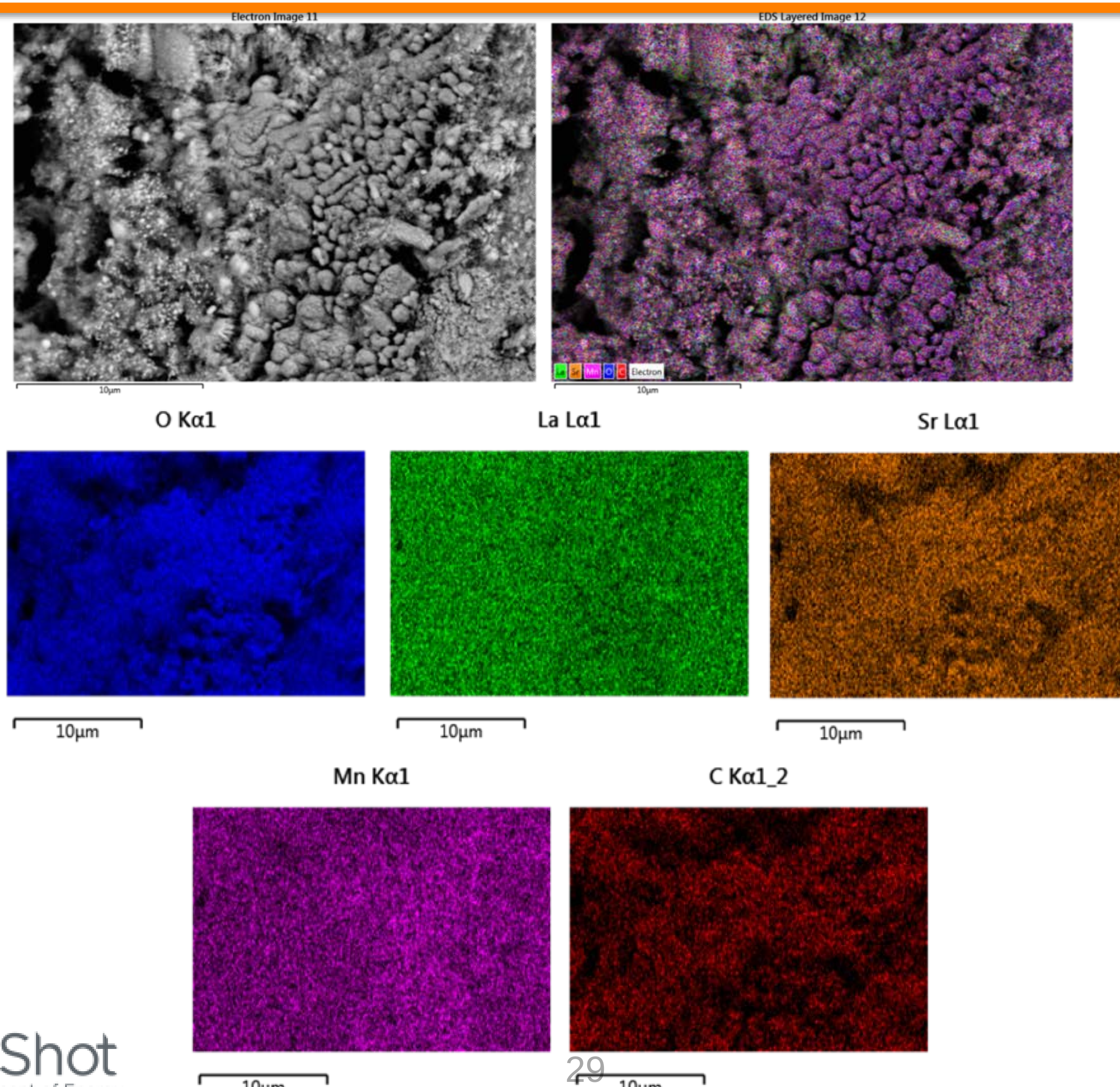
Aged LSM Re-deposition on Sidewalls





- Crystallites are present on top of re-dep and on LSM "substrate"
- TEM required to identify the crystallites
- Crystallites result from diffusion

Aged LSM EDS Inconclusive

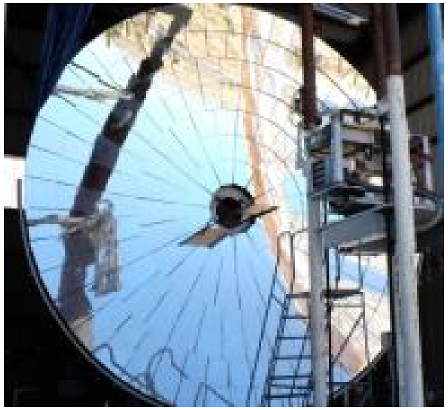


On-Sun Testing

Solar Furnace

National Solar Thermal Test Facility (NSTTF)

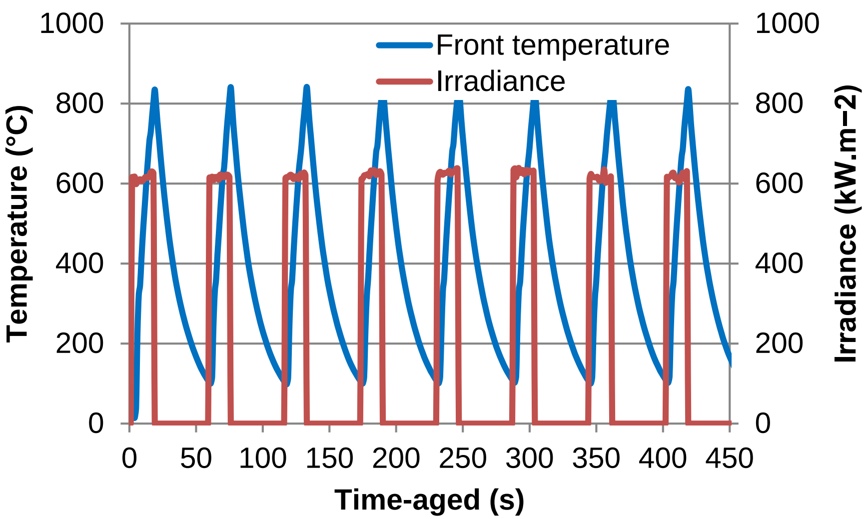


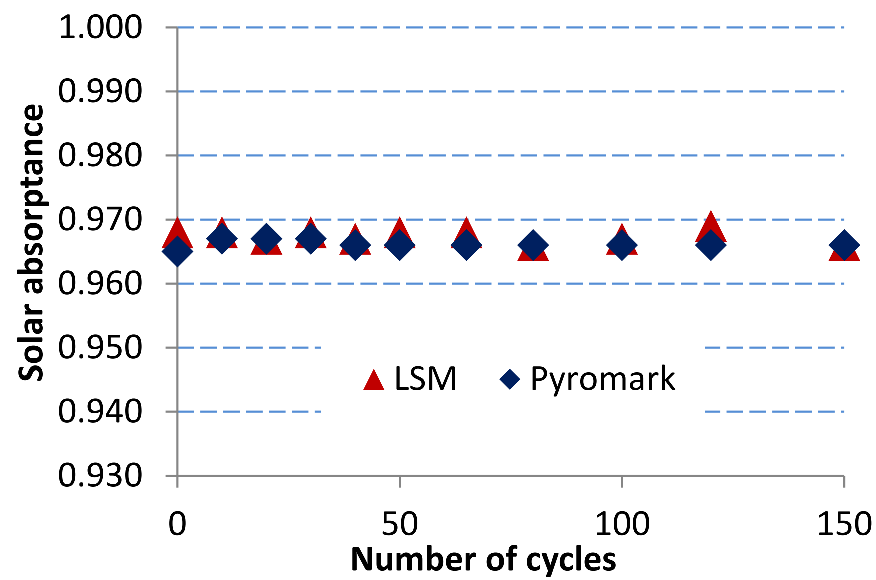




On-sun Testing LSM on Inconel 625

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 $\eta_{final} = 0.902$

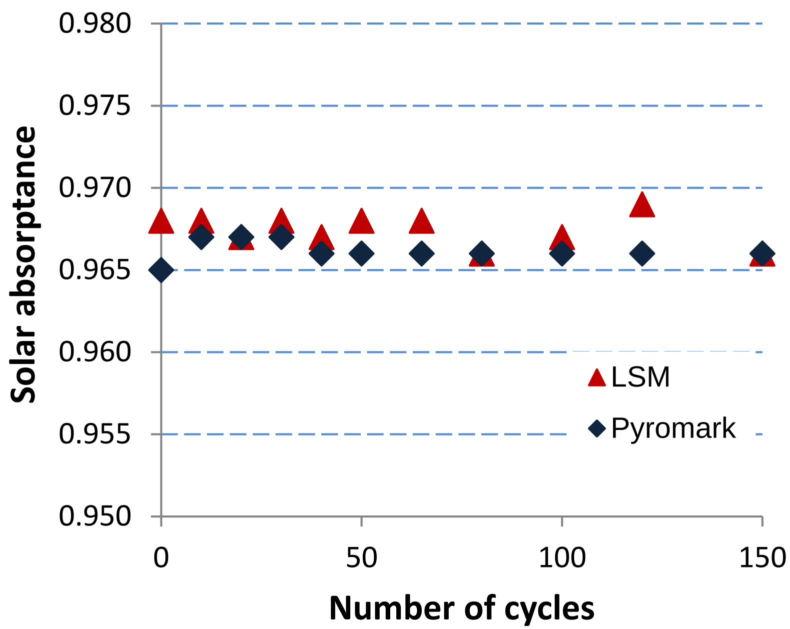
Pyromark $\eta_{final} = 0.893$

On-sun Testing

150 automatic heating/cooling cycles
Substrate: Inconel 625

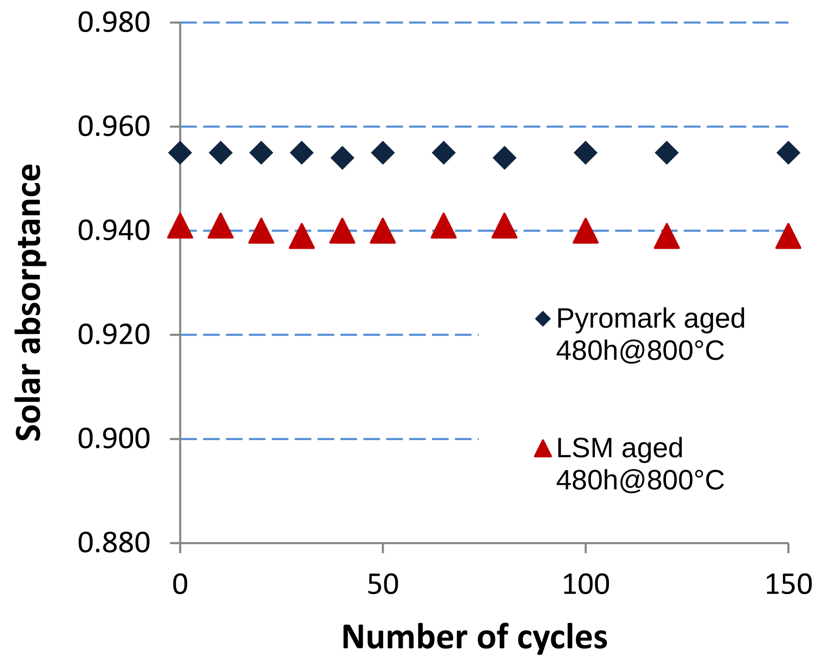
600 kW m^{-2} / 0 kW m^{-2}

700˚C / 100˚C



600 kW m^{-2} / 0 kW m^{-2}

850˚C / 100˚C



LSM η_{final} = 0.902
Pyromark η_{final} = 0.893

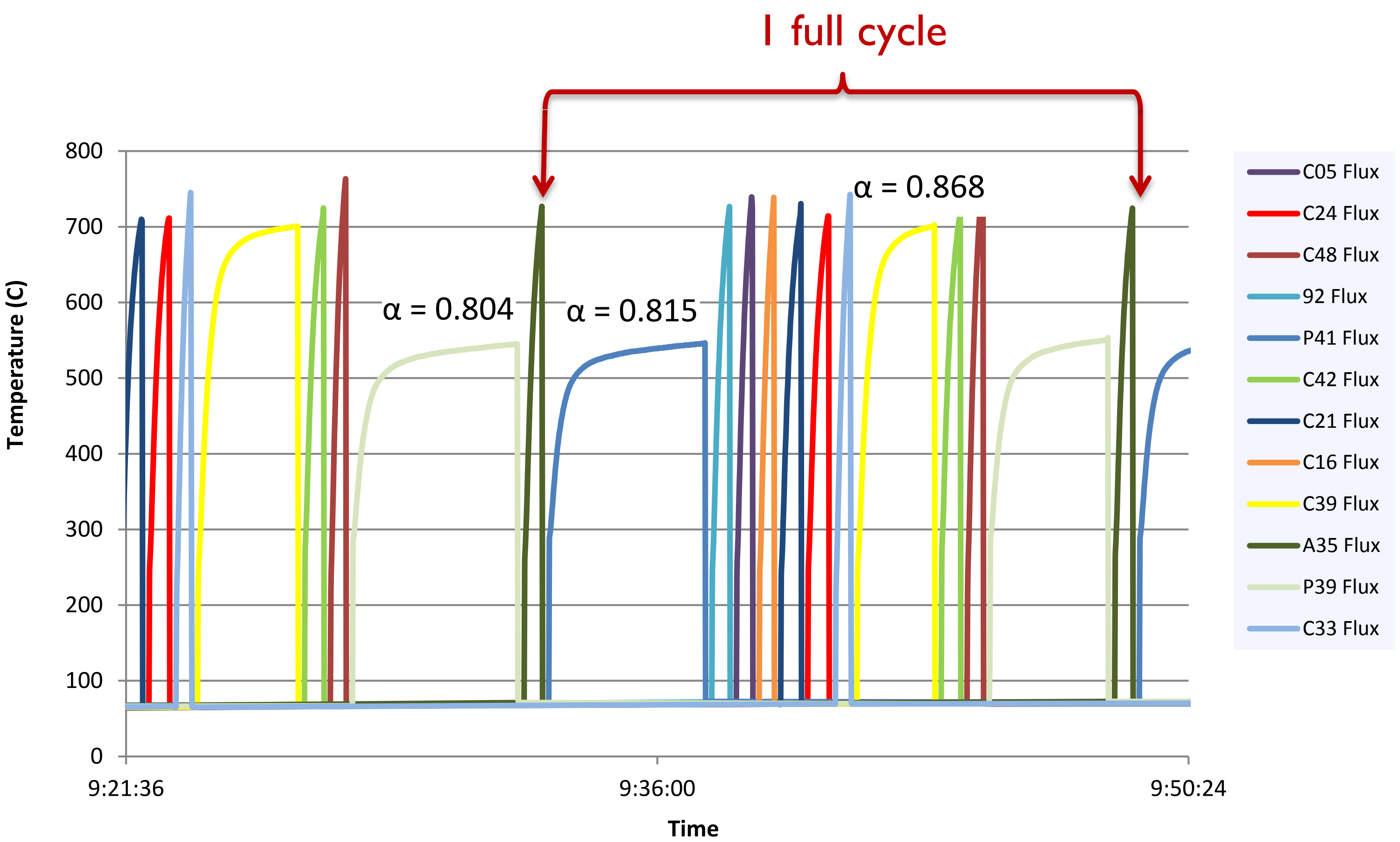
Pyromark η_{final} = 0.882
LSM η_{final}= 0.880

Automated Sample Handling and Exposure System (ASHES)

Solar Simulator Tests

Due to time constraints and complications with the sample holder, only 5-16 cycles were run

Full Cycle Solar Simulator



Most samples heat up within 25-40 seconds

Optical Properties Post-Simulator

				Before			Solar Sim (700 °C)			
Coupon #	**Thickness (Coatings)**	**Curing Rate (°C/min)**	**Curing Temp (°C)**	**α**	**ε**	**η_{sel}**	**α**	**ε**	**η_{sel}**	**# Cycles**
C05	3	5	750	0.969	0.877	0.896	0.954	0.863	0.882	11
C16	3	10	550	0.974	0.901	0.899	0.905	0.795	0.839	16
C21	3	15	550	0.973	0.897	0.898	0.947	0.823	0.878	11
C23	3	15	550	0.973	0.897	0.898	0.836		0.836	5
C24	3	5	650	0.970	0.900	0.895	0.836	0.768	0.772	13
C48	3	15	650	0.973	0.895	0.898	0.873	0.781	0.808	16
A35	NA	NA	LSM	0.990	0.953	0.911	0.969	0.909	0.893	16
A92	NA	NA	LSCF	0.980	0.926	0.903	0.968	0.920	0.891	16

- LSM appears stable, after limited number of cycles
- Decrease in values for Pyromark due to physical degradation of coatings
- Differs from on-sun testing results – possibly due to faster rate of heating/cooling
- Many more cycles required for verification

Summary

- Thermal-sprayed LSM that was surface modified using a laser treatment shows improved absorptivity
- Coatings show no sign of physical degradation and little degradation in absorptance after Isothermally aging at 600 °C/480 h
- Properties degrade at 700 – 800 °C
  - No structural changes seen in microscale (XRD, SEM)
  - However, on nanoscale some segregation and crystallization in troughs implied, which may be cause of decrease α but may also decrease ε
  - TEM and other characterization needed to confirm
- Preliminary on-sun tests at 700 °C also show good performance vs. Pyromark
- Preliminary solar simulator results show thermal sprayed coatings more physically stable than Pyromark
- High emissivity of the coatings remains a challenge
- Long-term testing and fundamental analyses of laser-treated samples necessary to determine mechanism of absorptance

Thank you for your attention.
Questions?