Refractory Solar Selective Coatings

Final Report

Applied Materials Division

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Final Report

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Executive Summary: This three-year project worked towards developing high-performance selective receiver coatings for concentrated solar power (CSP) to meet the DOE SunShot 2020 goal of levelized cost of energy (LCOE) ≤ 6 ¢/kWh. We exploited recent advances in photonic crystal fabrication and nanocomposite materials synthesis to manufacture coatings designed to withstand high operating temperatures in air (>800 °C) while maintaining a high solar absorptivity ($\geq 95\%$) and low IR emissivity ($\leq 10\%$). We engineered the selective receiver coatings at multiple length scales. In the $0.1\text{-}1\text{ }\mu\text{m}$ regime, the coating has a photonic crystal structure comprised of a periodic mesoporous array. This structure alters the photonic density of states to improve spectral selectivity while also mitigating thermal stress for improved lifetime. At the $1\text{-}10\text{ nm}$ scale, the coatings are composed of optically absorbing nanoparticles in a transparent matrix where the size, spacing, and composition of the nanoparticles are tailored to tune the optical properties for high visible absorption and low IR emittance - similar to a cermet, but with dramatically enhanced thermal stability. The photonic structure was fabricated by self-assembly from a nanoparticle suspension followed by infiltration using atomic layer deposition (ALD). The nanophase composite results by combining the ALD processes for a metal and a metal oxide.

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Background: Currently, the industry standard CSP coating is Pyromark 2500^{1, 3}. This coating is inexpensive (\$5/m²)³, and has a high solar absorbance of 0.96. However, Pyromark 2500 will not achieve the 2020 SunShot Targets for several reasons: the relatively high thermal emittance of 0.87 reduces the thermal efficiency at higher surface temperatures, and the coatings are not stable in air above ~650°C. The highest thermal efficiencies by far are achieved by cermet coatings composed of metallic nanoparticles embedded in an insulating, dielectric matrix. By varying the composition and proportions of the metal and matrix components, the cermet optical properties can be tuned precisely to maximize solar absorbance and minimize thermal emittance. Typical cermet coatings employ 2-4 homogenous cermet layers or a single, graded cermet layer, and are capped with an antireflective coating^{5, 6}. For instance, Mo-Si₃N₄ multilayer cermet coatings achieve a solar absorbance of 0.93 and a thermal emittance of 0.017, and would yield an unrivaled thermal efficiency of 0.93 at 1000°C (Table 1). Unfortunately, the cermet metals oxidize at temperatures of only 400°C and become transparent. In addition, cermets are prepared using physical vapor deposition and thus cannot be deposited on tubular receivers or within porous volumetric receivers⁷. Selective absorber materials with extreme high temperature durability and oxidation resistance, such as spinel oxide materials, are under development⁸. For example, researchers at UC San Diego have recently developed “black oxide” coatings consisting of cobalt oxide (Co₃O₄) nanoparticles prepared by solution-based methods. These coatings show an impressive thermal efficiency of 88% after 1000h heating at 750°C in air⁹. Ultimately, however, such coatings will be limited by the non-ideal optical properties intrinsic to these pure materials. One method to tune the optical properties of a material is by introducing controlled porosity to exploit photonics. This capability was recently demonstrated by tungsten inverse opal structures that were fabricated to provide an absorptivity of ~0.9 and an emissivity of ~0.1 by virtue of the suppressed thermal emission provided by the 3D structure². Although this provides an elegant proof-of-concept, tungsten is easily oxidized and so is not suitable for ambient CSP receivers. More complex nanostructures are under consideration as selective absorber coatings, but it remains to be seen if these materials can be produced cost effectively¹⁰.

The coating design that we developed in this project combines the best attributes of the aforementioned technologies. Similar to the cermets, our coatings are a nanocomposite of absorbing nanoparticles in a dielectric matrix so that the optical properties (n, k) are broadly tunable. Instead of the metallic nanoparticles used in cermets however, we adopt the approach used in the black oxide coatings and utilize refractory metal oxide and carbide absorbers to provide high temperature resistance to oxidation. In addition, we exploit the photonic enhancement demonstrated by the tungsten inverse

Selective Absorber Coating	Solar Absorptivity	Thermal Emissivity	Selective Solar Efficiency (η_{sel})			Max T(°C)	Tunable (n,k)?	Photonic enhancement?	Conformal Coating?
			T=650°C	T=720°C	T=1000°C				
Cermet (Mo-Si ₃ N ₄)	0.93	0.017	0.93	0.93	0.93	400	Y	N	N
Pyromark 2500	0.96	0.87	0.92	0.91	0.83	650	N	N	N
Black Oxide	0.92	0.80	0.89	0.88	0.80	750	N	N	N
Our Coating (targets)	>0.95	<0.10	0.95	0.94	0.93	>1000	Y	Y	Y

Table 1: Comparison of selective absorber coating technologies. Selective solar efficiency is calculated from ref¹ assuming Q=1000 kW/m² (~1000 suns). Values in red indicate that the temperature is beyond the range of thermal stability for the material. Only Black Oxide and our coatings will achieve the SunShot Target of ≥90% thermal efficiency at 720°C.

opal films, allowing additional control over the optical properties to suppress infrared emission. Finally, by utilizing atomic layer deposition (ALD) to deposit our coatings, we are able to conformally coat the outside of long tubes for liquid receivers, or the inner surfaces of a porous monolith such as silicon carbide foam for volumetric air receivers. All of these advantages are summarized in Table 1.

Introduction: This project developed refractory solar selective coatings intended to meet or exceed all of the SunShot Targets for Receiver Subsystems: cost $\leq \$150/\text{kW}_{\text{th}}$, thermal efficiency $\geq 90\%$, exit temperature $\geq 720^\circ\text{C}$, and lifetime $\geq 10,000$ cycles. Our technology combines the best attributes of previous solar selective coating strategies, while simultaneously overcoming their limitations. We used atomic layer deposition (ALD) nanocomposite coatings with low thermal emissivity and high solar absorptivity, similar to cermet⁵. However, unlike conventional cermets prepared by physical vapor deposition, ALD is highly conformal and permits the infiltration of porous photonic crystal structures. In addition, we will utilize 3D periodic mesostructures, established through modeling, to tune the optical behavior². However, unlike previous attempts using readily oxidized W, and unlike conventional cermets, our ALD nanocomposite has dramatically improved oxidation resistance, and higher spectral selectivity. Finally, we will adopt the Sandia approach of using naturally occurring refractory materials to avoid oxidation at high temperatures⁸, but blended these materials into nanocomposites that outperform natural materials. Although our primary target application was “power tower” CSP, our coatings are also applicable to parabolic trough and linear Fresnel systems.

The advantages of our technology can be understood using the efficiency for selective absorbers¹:

$$\eta_{sel} = \frac{\alpha_s Q - \varepsilon \sigma T^4}{Q} \quad (\text{Eq. A})$$

where α_s and ε are the wavelength-dependent absorptivity and emissivity of the coating, respectively, Q is irradiance on the receiver (W/m^2), σ is the Stefan-Boltzmann constant, and T is the receiver surface temperature (K). For maximum thermal efficiency we should have $\alpha_s=1$ over the solar spectrum and $\varepsilon=0$ in the infrared (Fig. A). Carnot’s theorem dictates that CSP plants become more efficient at higher operating temperatures, but this places intense demands on the absorber coating: (1) Low emissivity becomes critical due to the T^4 term in Eq. A; (2) The black body curve shifts to shorter wavelengths and overlaps the solar spectrum (Fig. B); (3) The coating degrades through restructuring and oxidation; (4) The magnitude of diurnal temperature cycling increases, imposing greater thermomechanical stresses that delaminate and disintegrate the coating. Our coatings address each of these demands: (1) By controlling the photonic structure we optimize the cutoff

wavelength and reduce the emissivity^{2, 11, 12}. (2) Our nanocomposite coatings are composed of conducting 1-2 nm nanoparticles embedded in an amorphous matrix¹³⁻¹⁵ and tuning the size, spacing, and composition of the nanoparticles in the composite lends exquisite control over the α_s and ϵ spectra as shown in Fig. B. (3) The absorbing nanoparticles are composed of refractory carbides and oxides with extreme resistance to oxidizing conditions at high temperatures (Fig. C). (4) The mesoporous structure provides additional control over α_s and ϵ , and lends extreme stability for high temperature cycling, as we have demonstrated under vacuum conditions up to 1500°C¹⁶. This project will develop solar selective coatings for use in CSP “power tower” receivers. In particular, we will focus on tubular liquid receivers, and volumetric air receivers composed of a silicon carbide foam. Each technological aspect of our program is described below.

Nanocomposite Films: Prior to this CSP project, Argonne developed and commercialized nanocomposite films composed of conducting nanoparticles in a dielectric matrix for applications in electronics and detectors^{17, 18}. We discovered that these films are extremely promising candidates for refractory solar selective coatings because the optical properties are easily tuned (Fig. 3) and they are stable at high temperatures in air (Fig. 3). These nanocomposite films are deposited using atomic layer deposition (ALD), a thin film coating technology used in the high volume manufacturing of consumer electronics. ALD uses alternating exposures between pairs of gaseous precursor vapors (A and B) and a solid surface^{19, 20}. Repeating these exposures (ABAB...) deposits films in an atomic layer-by-layer fashion.

The chemical reactions between the precursor vapors and the surface are self-limiting – they naturally terminate when all reactive surface sites are consumed. This attribute distinguishes ALD from all other coating technologies and enables uniform coatings with atomic-level control over thickness and composition, even inside of mesoporous materials such as photonic scaffolds (Fig. 1). By switching between the pair of precursors to grow one material (AB) and the precursors for a different material (CD), novel materials can be created that are blended at the atomic scale. For instance, the nanocomposite films in Figs. B and C were synthesized by switching between the ALD precursors for aluminum oxide (A=trimethyl aluminum, B=H₂O), and those for tungsten (C=tungsten hexafluoride, D=disilane)^{14, 21-}

²³. The metallic nanoparticles form spontaneously through sintering during film growth. In this program, we evaluated a range of conducting nanoparticles (metals, carbides, oxides of W, Mo, Nb, Ta, and Co) and matrix materials (Al₂O₃, TiO₂, Ta₂O₅, ZrO₂, and

MgO). Prior to this project, the ALD precursor chemistries have been established for each of these materials, but most of the nanocomposites blends have not yet been created or characterized. For this work, we used Haynes 230 as the underlying substrate as this alloy is representative of those used in molten salt receivers and it is readily available in coupon form. The ALD films used conducting nanoparticle loadings of 5%-90% and thicknesses of 50nm-500nm.

Photonic Scaffolds: Photonic scaffolds were fabricated using xerogel, drop- and dip-casting methods, and 3D printing. Ordered and random porous scaffolds were generated from sol-gel and organically modified silicate precursors using monodisperse polystyrene and polymethylmethacrylate nanoparticles as sacrificial materials. Target values for the pore size (0.1-10 μm), scaffold thickness (1-1000 μm), and pore structure (opal, inverse opal, and random²⁴⁻²⁶) were provided by computer modeling using the finite difference time domain (FDTD) method²⁷. This modeling used MEEP, a free FDTD simulation software package developed at MIT to model electromagnetic systems. Modeling yielded the reflectivity based on the input scaffold geometry and the refractive index of the nanocomposite film and the underlying substrate (measured by ellipsometry), allowing calculation of α_s and ϵ . Fig. D shows preliminary results for an inverse opal scaffold obtained using MEEP. The photonic scaffolds will be infiltrated with the ALD nanocomposite films to yield the refractory solar selective coatings. In some cases, the scaffolds were removed by high temperature oxidation or solvent. In other cases, the scaffolds were retained in the final coating.

Figure D: FDTD modeling predicts 4x lower IR emissivity for photonic coating compared to dense coating of same material.

Summary of Tasks:

- Task 1.1: Develop Nanocomposites
 - Subtask 1.1.1: Deposit Nanocomposites – Test matrix will combine 5 nanoparticle metals (W, Mo, Nb, Ta, Co) and 5 dielectric matrix materials (Al_2O_3 , TiO_2 , Ta_2O_5 , ZrO_2 , and MgO) prepared by ALD. Utilize design of experiments (DoE) methodology to guide our survey.
 - Subtask 1.1.2: Measure Optical Properties - characterize optical and physical properties of these films using UV-Vis-NIR and ellipsometry.
 - Subtask 1.1.3: Down Select Nanocomposites – calculate selective absorber efficiency using Eq. A using criterion $\eta_{\text{sel}} \geq 0.85$.
- Task 1.2: Develop Photonic Scaffolds
 - Subtask 1.2.1: Model Photonic Scaffolds – Couple FDTD model to an optical model of the ALD nanocomposite films to help optimize the optical properties of the selective coatings.
 - Subtask 1.2.2: Fabricate Porous Scaffolds – Using photonic scaffold structures predicted in Subtask 1.2.1, fabricate scaffolds using xerogel, drop- and dip-casting methods, and 3D printing.
 - Subtask 1.2.3: Infiltrate Porous Scaffolds. Using the nanocomposites from Task 1.1, infiltrate porous scaffolds.
 - Subtask 1.2.4: Measure Optical Properties. Evaluate optical reflectivity, $R(\lambda)$, for selective solar coatings using UV-Vis-NIR spectrophotometry.
 - Subtask 1.2.5: Down Select Porous Scaffolds - Calculate selective absorber efficiency using Eq. A using criterion $\eta'_{\text{sel}} \geq 0.91$
- Task 1.3: Thermal Testing
 - Subtask 1.3.1: Isothermal Testing – Using selective absorber films from Task 1.2, heat in furnace at constant temperature of 650°C in air for 24 hours.
 - Subtask 1.3.2: Thermal Cycling – Perform 10 thermal shock cycles in furnace from 25-650°C in air.
 - Subtask 1.3.3: Measure Optical Properties – Evaluate optical reflectivity, $R(\lambda)$, for selective solar films.
 - Subtask 1.3.4: Measure Adhesion – Use tape test (ASTM D3359) and quantify P, percentage of film remaining intact.
 - Subtask 1.3.5: Down select coatings – Calculate selective absorber efficiency after isothermal testing using Eq. A. Use criteria $\eta'_{\text{sel}} \geq 0.91$ and $P \geq 99\%$.
- Task 1.4: Commercialization Plan Development

- Subtask 1.4.1: Technoeconomic Analysis: Estimate cost of coating receiver tubes.
- Subtask 1.4.2: Industrial Outreach – Establish and strengthen contacts with major CSP developers.
- Task 2.1: Environmental Testing
 - Subtask 2.1.1: Sample Preparation. Using 10 selective absorber coatings developed in Budget Period 1, deposit coatings on 6 different metal alloy coupons (60 total samples).
 - Subtask 2.1.2: Isothermal Testing. Perform furnace testing of 60 samples at constant temperature of 800°C in air for 24 hours. Measure optical and adhesion properties as described in Subtask 2.1.7-2.1.8. Select 15 samples for further testing in Subtasks 2.2.3-2.21.6 based on these measurements.
 - Subtask 2.1.3 Damp Heat Test. Subject samples to 85°C and 85% RH, IEC 62108, 1000 hours.
 - Subtask 2.1.4 Neutral Salt Spray Corrosion Test. Subject samples to test ISO 9227, 480 hours.
 - Subtask 2.1.5 UV-Light and Humidity Test. Subject samples to test ISO 11507, 1000 hours.
 - Subtask 2.1.6: Thermal Cycling. Perform 10,000 thermal shock cycles in furnace to $T_{max}=800^{\circ}\text{C}$ in air.
 - Subtask 2.1.7: Measure Optical Properties. Evaluate optical reflectivity, $R(\lambda)$, for selective solar coatings using UV-Vis-NIR spectrophotometry in wavelength range 250–2500 nm and FTIR reflectometry in wavelength range 1.1-15 μm . Calculate η'_{sel} , using Eqns. 1-3. Perform duplicate measurements (≥ 5), to allow evaluation according to the Assessment Tool.
 - Subtask 2.1.8: Measure Adhesion. Measure adhesion using tape test (ASTM D3359) on coatings after isothermal and environmental testing and quantify P, the percentage of the film that remains intact. Perform duplicate measurements (≥ 5), to allow evaluation according to the Assessment Tool.
 - Subtask 2.1.9: Improve Coating Uniformity. Measure η'_{sel} at 5 spatial locations for each of 5 coated samples prepared under identical conditions. Calculate the standard deviation in η'_{sel} values within each sample (σ_1) and between the samples (σ_2). Adjust coating parameters to achieve $\sigma_1 \leq 5\%$ and $\sigma_2 \leq 5\%$.
 - Subtask 2.1.10: Down selection. From initial 60 samples (10 coatings, 6 substrates), down select to 15 after isothermal testing; down select to 5 samples after climate chamber testing. Down selection is based on the evaluation criteria $\eta'_{sel} \geq 0.91$, $P \geq 99\%$, and $\sigma_1, \sigma_2 \leq 5\%$.

- Task 2.2: Long Term Isothermal Testing
 - Subtask 2.2.1: Sample Preparation. Using 5 highest performing selective absorber coatings identified in Task 2.1, deposit coatings on metal alloy coupons.
 - Subtask 2.2.2: Isothermal Testing. Perform furnace testing of 5 samples at constant temperature of 800°C in air for 4500 hours. (Note: keep duplicate samples in oven after completion of Budget Phase 2 to facilitate very long-term testing in Budget Phase 3.)
 - Subtask 2.2.3: Measure Optical Properties. Evaluate optical reflectivity, $R(\lambda)$, for selective solar coatings using UV-Vis-NIR spectrophotometry in wavelength range 250–2500 nm and FTIR reflectometry in wavelength range 1.1-15 μm . Calculate η_{sel} , using Eqns. 1-3. Perform duplicate measurements (≥ 5), to allow evaluation according to the Assessment Tool.
 - Subtask 2.2.4: Measure Adhesion. Measure adhesion using tape test (ASTM D3359) on coatings after isothermal and environmental testing and quantify P, the percentage of the film that remains intact. Perform duplicate measurements (≥ 5), to allow evaluation according to the Assessment Tool.
 - Subtask 2.2.5: Down selection. Calculate coating degradation rate (% efficiency/year) from (Eq. 4). Perform duplicate measurements (≥ 5), to allow evaluation according to the Assessment Tool. From the initial 5 samples, down select to 3 based on $D < 0.6\%$ and $P \geq 99\%$.
- Task 2.3: Commercialization Plan Development
 - Subtask 2.3.1: Calculate Absolute LCOC for Coatings. Calculate the absolute levelized cost of coating (LCOC) using methodology developed by A. Boubault et al. (Eq. 5).
 - Subtask 2.3.2: Create Industrial Outreach Survey. In Q1 of Budget Period 2, create a survey of questions that will be posed to each industry partner.
 - Subtask 2.3.3: Conduct Industrial Outreach: Formalize and strengthen contacts with 3-4 major CSP developers and producers. Establish NDAs, and conduct conference calls or face-to-face meetings with these companies. The success metric for this subtask will be to fill out the answer portion of the survey created in Subtask 2.3.2.

Project Results and Discussion:

Task 1.1: Develop Nanocomposites

A) Initial Studies Using W:Al₂O₃ Nanocomposites: The nanocomposites that we studied were combinations of 5 nanoparticle metals (W, Mo, Nb, Ta, Co), 5 dielectric matrix materials (Al₂O₃, SiO₂, Ta₂O₅, ZrO₂, and MgO), 10 metal compositions (5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% metallic component) and 4 film thicknesses (50, 100, 250, 500 nm) for a total of 1000 ALD materials. To tackle this large parameter space, we used a design of experiments (DOE) approach. Prior to beginning the DOE study, we performed some initial screening studies using ALD W:Al₂O₃ nanocomposite films to gauge the sensitivity of η_{sel} to the various parameters (thickness, metal:dielectric pair, metal %) in order to design an effective DOE.

Results: The ALD W:Al₂O₃ nanocomposite films were prepared with W cycle percentages ranging from 0-100% W using previously described methods^{14, 22}. Briefly, the W ALD was performed using alternating exposures to WF₆ and Si₂H₆ and the Al₂O₃ ALD used alternating exposures to trimethyl aluminum (TMA) and H₂O at a temperature of 200°C. The W cycle ratio is defined as $W\% = W/(W+Al_2O_3) \times 100$ where W and Al₂O₃ are relative number of WF₆/Si₂H₆ and TMA/H₂O ALD cycles performed, respectively. In the first set of films, we kept the number of successive ALD metal cycles at 1 (e.g. W=1, Al₂O₃=3 for the 25% W film). In the next set of films, we kept the cycle ratio at 25%, but varied the number of successive ALD W cycles (e.g. W:Al₂O₃=1:3, 2:6, 3:18 etc.). These films were characterized using spectroscopic ellipsometry (SE) and ultraviolet-visible-near infrared spectrophotometry (UV-Vis-NIR) to determine the optical properties including the bandgap. In order to correlate the optical properties with other physical and chemical properties of the films, we performed X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) measurements.

Figure 1: The density was determined by fitting XRR data for each of the films, and the relative W content was measured using XRF. Both the density and W content increase with W cycle ratio as expected. The non-linear increase in these quantities results from the inhibition of the W ALD on the Al₂O₃ surface.

Figure 1 shows the densities of the ALD W:Al₂O₃ nanocomposite films versus W cycle ratio as determined from XRR measurements performed on samples deposited on silicon substrates. The density increases with W% because of the increasing concentration of the heavier W in the lighter Al₂O₃ matrix with increasing W cycle ratio. This effect is

Figure 2: The density was determined by fitting XRR data for each of the films, and the relative W content was measured using XRF. Both the density and W content increase with W cycle ratio as expected. The non-linear increase in these quantities results from the inhibition of the W ALD on the Al₂O₃ surface.

corroborated by the XRF measurements (Fig. 1) which verify that the W content increases with increasing W%, and that the functional relationship between W content and density is very similar. The non-linear relationship between the W content and the W cycle ratio is a consequence of the ALD surface chemistries: the W ALD is inhibited on the ALD

Figure 3: Direct and indirect bandgap energies calculated from Tauc plots of UV-Vis absorption measurements versus W cycle ratio

Al₂O₃ surface. This behavior has been investigated previously using in situ quartz crystal microbalance and infrared absorption measurements^{14, 22}.

Next, we proceeded to measure the optical transmission (T) and reflection (R) of the ALD W:Al₂O₃ nanocomposite films prepared on fused silica substrates over the range W%=0-

60% using UV-Vis-NIR spectrophotometry. After subtracting the contributions from the substrate, the absorption coefficient, α for the films was calculated using:

$$\alpha = \frac{\log(1-T-R)}{t} \quad (1)$$

where t is thickness as determined from spectroscopic ellipsometry and cross-sectional SEM. Figure 2 shows the absorption coefficient values for the ALD W:Al₂O₃ nanocomposite films. The direct and indirect bandgaps were calculated from these measurements using Tauc-plots^{28, 29} and the results are shown in Fig. 3. These bandgap values were graphically calculated using the linear part of the absorption edge. The direct bandgap decreases from 5.2 eV to 4.2 eV between 10-40 W%, and the indirect bandgap decreases from 3.3 eV to 1.8 eV in the same range. Above 40%, the bandgap disappears, consistent with metallic behavior. The decrease in the direct bandgap with increasing W% likely results from the formation of localized W d-states within the Al₂O₃ bandgap as has been observed previously for other transition metals^{30, 31}. To explore this possibility, additional XPS studies were performed to determine the valence band structure of the nanocomposite films (Fig. 4). These measurements confirmed the interaction of W with the alumina matrix resulting in the formation of W 5d states hybridized with the oxygen 2p band near the valence band edge at about 2.6 eV (boxed region in Fig. 4). Earlier studies have correlated changes in the indirect bandgap of nanocrystalline tungsten oxide films with quantum confinement effects related to the size of the WO_x clusters³²⁻³⁴. Previously we established that the ALD W:Al₂O₃ nanocomposite films were comprised of metallic, 1-2 nm nanoparticles in an amorphous matrix. Consequently, we attribute the increase in indirect bandgap with W% to an increase in the size of the conducting nanoparticles in our films.

Figure 4: XPS spectra of ALD W:Al₂O₃ nanocomposite films showing valence band structure for W cycle ratios in the range of 0-100%.

We used spectroscopic ellipsometry to investigate the effect of composition on the optical constants (refractive index and extinction coefficient) of the ALD W:Al₂O₃ nanocomposite films. For materials comprised by two or more constituents or phases, it is often profitable to use effective medium theories such as those proposed by Maxwell-Garnett (M-G) and Bruggeman to obtain good approximations for the properties of the mixture, such as the volume fractions^{29, 35, 36}. We used the Bruggeman effective medium approximation (EMA) for the nanocomposite films with Al₂O₃ as the matrix modeled using a Cauchy dispersion model and W as the inclusion modeled using a B-spline formula. These models require accurate measurements of the optical constants for the individual constituent phases. Therefore, we first analyzed ellipsometric data for pure Al₂O₃ films using a Cauchy dispersion function, and for pure W using a Kramers-Kronig consistent Bspline function to obtain the optical constants for these films. The quality of the fitting was verified by noting that the mean squared error (MSE) for several sets of films having the same W% and increasing thickness was <3.

Figure 5 shows the optical properties derived from fitting the ellipsometric data to the model described above. The insets to Fig. 5 show expanded regions for the 0-40 W% films. The final fits showed only one local minimum and had MSE < 3 for all cases where W% < 40 indicating that the ALD nanocomposite films are accurately described using the EMA model in this range of compositions. This agreement is consistent with previous high-resolution cross-sectional TEM images of the 30% film, which showed well-dispersed, small particles, distributed in an amorphous matrix^{14, 22, 37}. For W% ≥ 50 the EMA model did not converge to a single local minimum, implying that the material was no longer composed of well-dispersed nanoparticles in an amorphous matrix. This behavior is evident in Fig. 5, where the n and k values begin to increase versus wavelength at W% ≥ 50. For the ALD W:Al₂O₃ nanocomposite films having W% ≥ 50, a Kramers-Kronig

consistent Bspline function was used to extract the optical constants by fixing the thickness and surface roughness values as measured by scanning electron microscopy and X-ray reflectivity, respectively.

The absorption coefficient data (Fig. 2) can be used to calculate the efficiency for selective absorbers¹:

$$\eta_{sel} = \frac{\alpha_s Q - \varepsilon \sigma T^4}{Q} \quad (2)$$

where α_s and ε are the absorptivity and emissivity of the coating, respectively, Q is irradiance on the receiver (W/m^2), σ is the Stefan-Boltzmann constant, and T is the receiver surface temperature (K). For maximum thermal efficiency we should have $\alpha_s=1$ over the solar spectrum and $\varepsilon=0$ in the infrared. The absorptivity can be calculated from:

$$\alpha_s = \frac{\int_0^\infty A(\lambda) G(\lambda) d\lambda}{\int_0^\infty G(\lambda) d\lambda} \quad (3)$$

where $A(\lambda)$ is the absorbance of the film (equal to be $1-R(\lambda)$, the reflectivity in the thick-film limit), and $G(\lambda)$ is the ASTM AM1.5D solar spectral irradiance; and the emissivity can be calculated from:

$$\varepsilon = \frac{\int_0^\infty A(\lambda) L(T, \lambda) d\lambda}{\int_0^\infty L(T, \lambda) d\lambda} \quad (4)$$

where $L(T, \lambda)$ is the black body emission Planck function⁶. We calculated the absorptivity,

Figure 6: Thermal emissivity and selective solar efficiency for ALD W:Al₂O₃ nanocomposite films versus W cycle percentage calculated from the absorption coefficient data in Fig. 2. These calculations assume $T=973K$ and $Q=5 \times 10^5 W/m^2$ (500 Sun concentration factor).

emissivity, and selective solar efficiency for our ALD W:Al₂O₃ nanocomposite films using Eqns. 2-4 and the absorption data in Fig. 2. For these calculations, we adjusted the film thickness to achieve $\alpha_s=0.98$, and we linearly extrapolated the absorption data to longer wavelengths for the emissivity calculation. We assumed $T=973K$ and $Q=5 \times 10^5 W/m^2$ (500 Sun concentration factor). The calculated emissivity (ε) and selective solar efficiency (ρ_{sel}) values are shown in Fig. 6. Figure 6 reveals that at cycle percentages of $W=10$ -

20%, the emissivity is relatively high and the efficiency relatively low. Due to the higher bandgap, these films are relatively transparent in the visible range and consequently must be very thick (30-45 microns) to achieve $\alpha_s=0.98$, and this increases the IR absorbance. The W=60% also has a high emissivity and low efficiency but for a different reason. The metallic nature of this film provides a relatively flat absorption spectrum (Fig. 6) and the IR absorption leads to a lower efficiency. However, for the films of intermediate metal content (W=30-50%), the combination of high visible absorption and low IR absorption yields low emissivities of 0.23-0.28, and high efficiencies of 0.95-0.96. These results suggest that the W=30-50% films have favorable optical properties to serve as selective solar absorbing coatings for CSP receivers.

Next, we prepared a series of ALD W:Al₂O₃ nanocomposite films keeping the W cycle percentage constant at 25%, but increasing the number of ALD W cycles performed in succession. For instance, the 25% W films can be prepared using 1, 2, or 3 ALD W cycles performed consecutively by following them with 3, 6, or 12 consecutive ALD Al₂O₃ cycles, respectively. These films were characterized using UV-Vis-NIR, and the data were analyzed using the same procedure described above to calculate the emissivity (ϵ) and selective solar efficiency (ρ_{sel}) values and these results are plotted in Fig. 7 versus the

number of successive W ALD cycles. We see that the emissivity and selective solar efficiency are optimized for the films prepared using single ALD W cycles in the 25% W cycle percentage films. The absorption spectra for these films (not shown) reveal that the IR absorption increases with the number of successive W cycles, and this accounts for the increase in ϵ and drop in ρ_{sel} .

To explore the generality of the behavior observed in Figure 7, we prepared a series of ALD Mo:Al₂O₃ nanocomposite films. The Mo ALD was performed using alternating

exposures to MoF_6 and Si_2H_6 at a temperature of 200°C . In this series, we kept the Mo cycle percentage constant at 10%, but increased the number of ALD Mo cycles performed in succession. Note that the 10% Mo films yield approximately the same metal content as the 25% W films as a result of the larger growth per cycle of ALD Mo ($10 \text{ \AA/cycle}$) as compared to ALD W ($4 \text{ \AA/cycle}$) under these growth conditions. These films were characterized using UV-Vis-NIR, and the data were analyzed using the same procedure described above to calculate the emissivity (ϵ) and selective solar efficiency (ρ_{sel}) values and these results are plotted in Fig. 8 versus the number of successive Mo ALD cycles. We see that the behavior for the ALD Mo: Al_2O_3 nanocomposite films using 10% ALD Mo cycles is very similar to that of the ALD W: Al_2O_3 nanocomposite films using 25% ALD W cycles versus the number of ALD successive ALD metal cycles. The thermal emissivity is lowest and the selective solar efficiency is highest for the films prepared using single ALD Mo cycles in the 10% Mo cycle percentage films. The magnitude of the increase in emissivity and decrease in selective solar efficiency is larger in the case of Mo compared to W, and this is attributed to the higher growth per cycle of the ALD Mo compared to the ALD W. We attribute the behavior in Fig. 8 to the increase in IR absorption with the number of successive Mo cycles.

Discussion: The results shown in the previous sections are consistent with a transition at $W\% \sim 50$ from dielectric to metallic behavior for the ALD W: Al_2O_3 nanocomposite films. Below $W\% = 50$, the refractive index shows a weak, decreasing dependence with wavelength (Fig. 7), a feature common to dielectric materials in which the dielectric constant in the visible range is dominated by the high energy interband transition between the conduction and the valence bands. The fact that the optical properties of these films can be fit well using an effective medium approximation (EMA) model is consistent with a nanocomposite structure comprised of a conducting phase embedded in a dielectric matrix. This interpretation is supported by previous TEM measurements^{14, 22, 37}

It is interesting to compare our ALD W: Al_2O_3 nanocomposite films with previous cermet materials. In our work, the optical properties for the ALD W: Al_2O_3 nanocomposite films with $W\% < 50$ were well fit using an EMA model, but for W: Al_2O_3 cermets prepared by physical vapor deposition (PVD) this was not the case³⁸. A key difference is that the 1-2 nm particles in our ALD films are substantially smaller than those seen in some PVD cermets. Consequently, the main requirement for Bruggeman's EMA mode, (homogeneity at a scale below optical wavelengths) is better satisfied in our case. The practical implication is that the broad optical tunability does not come at the expense of increased scattering, which is often a major limitation in the application of composite materials to optics. Another practical implication is that the optical properties of the nanocomposite films for any metal % can be easily calculated from the measured refractive indices (n , k) of the pure components, so long as the metal % is below the dielectric to metallic transition point for the composite. Finally, Figs. 7 and 8 demonstrate that the selective solar efficiency is highest for a given metal cycle percentage using only single, individual ALD metal cycles rather than multiple metal ALD cycles in succession.

B) Design of Experiments: The previous section explored the ALD W-Al₂O₃ nanocomposite films and yielded the following insights regarding ALD nanocomposites for selective solar absorbing coatings:

- 1) η_{sel} is maximized in the range of 20-50% W cycle ratio, so compositions outside of this range can be ignored.
- 2) η_{sel} is independent of thickness. This is because η_{sel} be calculated for any thickness once the refractive index (n, k) for the nanocomposite is known, and (n,k) are independent of thickness
- 3) The refractive index (n, k) for the nanocomposites can be well-modeled using an effective medium approximation (EMA) model. The EMA model takes as input (n, k) for the pure metal and dielectric components, and calculates (n, k) for any %W cycle value

Consequently, in order to determine η_{sel} for the full 5x5 matrix of candidate materials in this program, we *propose* that it is sufficient to:

- a) Measure (n, k) for each of the pure compounds (the 5 metals and the 5 dielectrics)
- b) Use the EMA model to calculate (n, k) for nanocomposites in the range 20-50% metal ratio.
- c) Calculate η_{sel} over this range and select the maximum value

Experiment run	Run order	metal: dielectric (m:d)	Thickness (nm)	Metal cycles (%)	average selective absorber efficiency values, (η_{sel})				
1	1	W:Al ₂ O ₃	20 (-)	20 (-)	0.9474	0.9489	0.9486	0.9489	0.9491
2	4	W:Al ₂ O ₃	20 (-)	60 (+)	0.8802	0.8803	0.8799	0.8799	0.8801
3	2	W:Al ₂ O ₃	100 (+)	20 (-)	0.9128	0.9107	0.9118	0.9058	0.9087
4	3	W:Al ₂ O ₃	100 (+)	60 (+)	0.8887	0.8890	0.8892	0.8893	0.8887
5	7	W:ZrO ₂	20 (-)	25 (-)	0.9464	0.9468	0.9472	0.9474	0.9479
6	5	W:ZrO ₂	20 (-)	75 (+)	0.8933	0.8931	0.8931	0.8937	0.8934
7	6	W:ZrO ₂	100 (+)	25 (-)	0.9039	0.9054	0.9028	0.9030	0.9023
8	8	W:ZrO ₂	100 (+)	75(+)	0.8843	0.8842	0.8850	0.8852	0.8850
9	11	Nb:Al ₂ O ₃	20 (-)	20 (-)	0.9480	0.9395	0.9488	0.9435	0.9519
10	12	Nb:Al ₂ O ₃	20 (-)	80 (+)	0.8980	0.8974	0.8974	0.8970	0.8969
11	10	Nb:Al ₂ O ₃	100 (+)	20 (-)	0.9007	0.9037	0.9032	0.9084	0.9117
12	9	Nb:Al ₂ O ₃	100 (+)	80 (+)	0.8875	0.8877	0.8877	0.8877	0.8877
13	15	Nb:ZrO ₂	20 (-)	20 (-)	0.9500	0.9500	0.9501	0.9502	0.9501
14	14	Nb:ZrO ₂	20 (-)	80 (+)	0.8946	0.8940	0.8946	0.8942	0.8939
15	13	Nb:ZrO ₂	100 (+)	20 (-)	0.9492	0.9497	0.9498	0.9497	0.9496
16	16	Nb:ZrO ₂	100 (+)	80 (+)	0.8881	0.8883	0.8883	0.8882	0.8883

Table 1: List of experimental runs for DOE study of ALD nanocomposite films. Experimental results are given in blue

This methodology (a-c) assumes that the results (1-3) are robust, and that they are valid for all of the materials combinations. We will scrutinize these assumptions using DOE. Our DOE will consist of three factors: thickness, metal cycles, and metal:dielectric pair.

We will use two levels for thickness: 20 (low) and 100 (high). These levels were selected to bracket the practical range of ALD film thicknesses for our application in CSP. We will use two levels for metal cycles: 20% (low) and 80% (high) where the low level is selected to be inside the anticipated range of maximum η_{sel} (20-50%) and the high level is selected to be outside of this range. Finally, we will use 4 levels for the metal:dielectric pair: W:Al₂O₃, W:ZrO₂, Nb:Al₂O₃, and Nb:ZrO₂. These levels were selected to be a manageable subset of the full 5x5 materials matrix that includes different dielectrics with the same metal and vice versa. The list of experimental runs is given in Table 1.

The run order was selected to be random within a given metal:dielectric level, but to process all of the samples in each metal:dielectric group together for experimental convenience (swapping precursors is time consuming). Each experimental run will generate 5 samples, and η_{sel} values will be measured for each of these samples. We will use these values to generate an ANOVA table as follows:

Source	SS	df	MS	F	F _{crit} (5%)	Result
m:d	0.0005030	3	0.0001677	0.6209294	2.75	True
thick	0.0012065	1	0.0012065	4.4682624	3.99	False
metal%	0.0074866	1	0.0074866	27.7260041	3.99	False
metal% x thick	0.0007314	1	0.0007314	2.7088068	3.99	True
m:d x thick	0.0020537	3	0.0006846	2.5352248	2.75	True
m:d x metal%	0.0083719	3	0.0027906	10.3349354	2.75	False
residuals	0.0172813	64	0.0002700			
totals		69				

Table 2: ANOVA table of DOE study of ALD nanocomposite films. Results of analysis are given in blue.

Where SS is the sum of squares, df is degrees of freedom, MS is mean square, F is the ratio of the level mean square and the residual mean square, which is compared to the tabulated F_{crit} value at the 5% confidence level to generate the result of the null hypothesis (true or false). In each case, the null hypothesis is that η_{sel} is independent of the source factor. In other words, a value of “true” indicates that the given factor (e.g. thickness) does not exert a statistically significant influence on the efficiency.

Results

A series of 80 ALD nanocomposite films on fused silica was prepared according to the list of experimental runs presented above. In each case, 5 duplicate films were prepared in each batch to gauge the statistical variation in the calculated η_{sel} values. The precursors used for each of the pure ALD materials were: W (WF₆/Si₂H₆); Nb (niobium pentafluoride, NbF₅/TMA); Al₂O₃ (TMA/H₂O); ZrO₂ (tetrakisdimethylamido zirconium (IV), TDMAZr/H₂O) and all depositions were performed at 200°C. In each case, The metal cycle ratio is defined as $M\% = M/(M+D) \times 100$ where M and D are relative number of metal and dielectric ALD cycles performed, respectively, and the number of successive ALD metal cycles is kept at 1. The films were characterized using spectroscopic

Figure 9: Photographs of W:ZrO₂ films prepared for DOE study.

Figure 10: Absorption coefficient versus wavelength for ALD Nb-Al₂O₃ nanocomposite films of thickness 20 nm (top row) and 100 nm (bottom row) and with metal cycle percentage of 20% (left column) and 80% (right column). Each graph shows the absorption coefficient versus wavelength for 5 duplicate samples as measured by UV-vis-NIR specular transmission and reflection, and was calculated using thickness values determined by spectroscopic ellipsometry.

ellipsometry (SE) and ultraviolet-visible-near infrared spectrophotometry (UV-Vis-NIR) to determine the optical properties and thickness, t . Both the diffuse reflectance (R) and the diffuse transmittance (T) were measured for each sample, and the absorbance was calculated as $A=1-R-T$. In each case the R and T of the fused silica was subtracted to yield the values for the ALD film, and the absorption coefficient was calculated using $\alpha=-\log(1-A)/t$. Figure 9 shows photographs of the W:ZrO₂ films prepared for the DOE study.

(rows 5-8 in Table 1). In each case, 5 fused silica samples were prepared along with one or more silicon samples. The yellow circles on the fused silica are pieces of Kapton used to mask one side of the substrate to ensure that the UV-vis measurements sample only one thickness of the ALD film. It is evident in Fig. 9 that the 100 nm and 75%W films are darker compared to the 20 nm and 25%W, respectively.

Figure 10 shows representative absorption coefficient measurements for the ALD Nb-Al₂O₃ nanocomposites. These data correspond to experimental runs 9-11 in the table above, using thickness 20 nm (top row) and 100 nm (bottom row) and with metal cycle percentage of 20% (left column) and 80% (right column). Each graph shows the absorption coefficient versus wavelength for 5 duplicate samples as measured by UV-vis-NIR specular transmission and reflection, and was calculated using thickness values determined by spectroscopic ellipsometry. In all cases, the absorption is high in the UV

Figure 11: Absorption coefficient versus wavelength for ALD Nb-Al₂O₃ nanocomposite films of thickness 20 nm (top row) and 100 nm (bottom row) and with metal cycle percentage of 20% (left column) and 80% (right column). Each graph shows the absorption coefficient versus wavelength for 5 duplicate samples as measured by UV-vis-NIR specular transmission and reflection, and was calculated using thickness values determined by spectroscopic ellipsometry.

and decreases with increasing wavelength. However, in the 20% films (left column), the absorption decreases to zero whereas in the 80% case, the absorption decreases to a finite, non-zero value. This non-zero absorption is due to the metallic nature of these films deposited using a high Nb%. Next, these data were extrapolated to 5000 nm using an exponential decay fit to the trailing edge. The α_s and ϵ values were calculated using Eq. 1 and 2 with $T=973K$ and $Q=5 \times 10^5 \text{ W/m}^2$ (500 Sun concentration factor), and the thickness was adjusted to achieve $\alpha_s=0.98$. The resulting absorption spectrum for the first sample in the 20 nm, 20% Nb-Al₂O₃ experimental run are shown as the green curve in Fig. 11. Also shown are the normalized solar spectrum (blue) and the normalized blackbody radiation curve (red) for reference. Using these values, Eqns. 1-3 yield $\alpha_s=0.98$, $\epsilon=0.31$ and $\eta_{sel}=0.95$.

This process was repeated for all of the 80 ALD nanocomposite films in the DOE study and the resulting η_{sel} values are shown in blue in Table 1. We note that within a given experimental run, the η_{sel} are very consistent and show a standard deviation of $\sim 0.1\%$ from the mean of the experimental run on average. This demonstrates that the coating process and measurement protocol are very reproducible. An ANOVA analysis was performed on the data in Table 1 and the results are shown in blue in Table 2.

Discussion

Referring to Table 2, for the “metal:dielectric” factor, we found $F=0.6209 << F_{\text{crit}}(5\%)=2.75$ yielding a result of “true”. This finding implies that the choice of metal and dielectric pair has no significant influence on the resulting η_{sel} . In other words, from the standpoint of spectral selectivity, any of the 25 metal:dielectric pairs in this study can be considered a viable candidate for future development and that the down selection can be based on other properties of the film such as thermal stability, oxidation resistance and adhesion. For the “thickness” factor, $F=4.468 > F_{\text{crit}}(5\%)=3.99$ yielding a result of “false”. This implies that coating thickness has a small but statistically relevant influence on η_{sel} . Examining Table 1, we see that the η_{sel} values are slightly larger for all of the 20 nm coatings compared to their 100 nm counterparts. We believe that this difference stems from an artefact in the diffuse transmission measurements. For the thicker films, the transmission values were often close to the instrumental detection limit leading to a distortion in the measured absorption curves. This hypothesis could be validated by comparing films of different thickness having larger transmission values that are within the reliable range of the instrument. However we note that the effect is very small, and had we chosen a slightly more stringent criterion such as $F_{\text{crit}}(3\%)=4.93$, then the result would be “true”. The “metal cycles” factor gave $F=27.72 >> F_{\text{crit}}(5\%)=3.99$ yielding a result of “false”. This finding demonstrates that the M% value used when depositing the films is very significant in the measured η_{sel} value. Regarding the cross terms, both the “metal% x thickness” and “metal:dielectric factor x thickness” were found to be insignificant ($F_{\text{crit}}(5\%) > F$), whereas the “metal:dielectric factor x metal%” showed $F=10.3 >> F_{\text{crit}}(5\%)=2.75$ implying that this cross term has significant effect on η_{sel} , but it is a smaller effect than from metal% alone ($F=27.7$)

To summarize, the DOE study taught us that the film thickness and metal:dielectric pair are not significant for the spectral selectivity of the ALD nanocomposite films. Therefore, we are justified in modeling the optical constants for the nanocomposite films using an EMA model based on measured optical constants for the pure metal and dielectric components. This modeling is ongoing. On the other hand, the metal % is extremely important, and to a certain extent, the choice of metal% coupled with the metal:dielectric pair is important as well.

Task 1.2: Develop Photonic Scaffolds

A) Modeling of Photonic Scaffolds: In order to tune the optical properties of the refractory solar selective coatings, the ALD films will be deposited inside of mesoporous, photonic scaffolds. The photonic scaffold structure will alter the photonic density of states to improve spectral selectivity while also mitigating thermal stress for improved lifetime. This

photonic enhancement, combined with the intrinsic selectivity of the ALD nanocomposite coatings, will provide very high selective solar efficiencies. In order to generate target values for the pore size (0.1-10 μm), scaffold thickness (1-1000 μm), and pore structure

(opal, inverse opal, and random²⁴⁻²⁶) of the photonic scaffolds, we have created a computer model using the finite difference time domain (FDTD) method²⁷. This model makes use of MEEP, a free FDTD simulation software package developed at MIT to model electromagnetic systems. Modeling will yield the predicted reflectivity based on the input scaffold geometry and the refractive index of the nanocomposite film and the underlying substrate allowing calculation of α_{sel} and ϵ .

Using refractive index values from ellipsometric measurements from the ALD W:Al₂O₃ nanocomposite with 40% W cycles (which showed the highest α_{sel} in Fig. 6), we modelled hexagonally close packed opal structures using spheres of diameter of 1.2 μm and calculated the R and T values for these structures. Figure 12 shows the results of the modelling using 6-layers of opal (left) and 12-layers of opal (right) in a free-standing configuration. In each case, the upper graphs show the calculations for the opal structures, while the lower graphs show the results for corresponding flat samples (i.e. the same volume of ALD nanocomposite film, but without the void space that defines the opal structure). The figures demonstrate that the opal structure enhances the reflectivity by 3.5x for the 6-layer opal, and by 7.5x for the 12-layer opal, at the normalized frequency value of 0.5 corresponding to a wavelength of 1200 nm. These results demonstrate that we have established a methodology for computing the photonic enhancement, and that the IR reflectivity of the refractory solar selective coatings can be enhanced using the opal structure. This model will now be coupled to an optical model of the receiver material to help optimize the optical properties of the selective coatings.

In terms of the optical properties, we have generalized our model to consider materials with a dielectric constant composed of an arbitrary long array of Lorenz oscillators and a Drude term. We have applied this model to the simulation of a subset of the ALD nanocomposite materials, including the W:Al₂O₃ ALD composites in the range between 10% and 40%. In order to strengthen the connection between experiments and simulations, we have modified our code to directly take as an input the optical model files

that are obtained through the fitting of the spectroscopic ellipsometry. The optical model is then transformed into the non-dimensional expressions used by the FDTD code. Preliminary analysis of the 10%-40% W:Al₂O₃ films indicates that the photonic scaffolds can enhance the overall efficiency in two different ways: for low W%, they effectively reduce the absorption in the IR compared to the flat films. For high W%, we observe a reduction of the reflection losses in the visible range.

We also studied the impact of film thickness and number of layers in the inverse opal structure, and the results show that thickness in eggshell-type of structures can be used as an independent parameter to tune light absorption, with thickness to skin depth ratio being the relevant physical parameter. These results were obtained assuming a free-standing film with no underlying scaffold such as that shown in Figure 13a. In terms of the potential architectures, we have also extended the model to consider three different types of structures: in addition to the fcc 111 inverse opal films discussed above, we have implemented inverse egg-shell structures resulting from the thin film coating and subsequent etching of fcc 111 opals, and multilayer coated inverse opals in which the inverse opals are fully infiltrated and then conformally coated.

Finally, we took advantage of our ability to incorporate optical properties of real materials to validate our simulation code. As a first benchmark, we chose a 6-layer inverse opal of annealed ALD W eggshell structure. Both experimental and FDTD results of the resulting optical properties have been published in the literature². The agreement between our simulation results and the published experimental and simulation data is excellent (Figure 13). We are therefore confident that our models captures the physics of the interaction of

electromagnetic radiation with inverse scaffolds correctly. In the next period, we will focus on the direct validation of various scaffolds coated with ALD materials.

B) Fabrication and Characterization of Porous Scaffolds: We have two general structures for the porous scaffolds. The first is well-ordered inverse opal scaffolds fabricated using monodispersed nanospheres to generate uniform and defect-free films. These scaffolds are intended for optimal coupling between theory and experiment in order to validate the methodology of using photonic enhancement to improve selective absorber efficiency. The second strategy is randomly organized scaffolds prepared by a variety of techniques. Although not as easily modeled compared to the inverse opals, these random scaffolds are more likely to be manufacturable on receiver tubes.

1) Inverse Opal Silica Scaffolds: The inverse opal silica (IO-SiO₂) scaffolds were prepared according to the scheme in Figure 14³⁹. The synthesis was performed in four steps:

- (1) Preparation of standard TEOS solution. The standard TEOS solution was made by mixing 1.5 mL of EtOH, 1.0 mL of DI H₂O, 8.1 μ L of HCl (37 wt% stock) and 1.0 mL of TEOS. Stir at room temperature for 15 minutes prior to use;
- (2) 1.0 mL of colloidal PS sphere solution (variable diameters) was added to 20 mL of DI H₂O, and 0.2 mL of the standard TEOS solution prepared in step (1);
- (3) Substrate (glass slide/Si wafer/Haynes 230) was vertically suspended in the vial containing the PS/TEOS suspension solution prepared in step (2).
- (4) The solvent content was evaporated slowly over a period of 1–2 d in a 65 °C oven to allow the deposition of an opal thin film onto the suspended substrate. The films were then calcined in air at 500 °C for 2 h, with a 4 h ramp time to remove the PS polymer template and partially sinter the SiO₂ structure.

The IO-SiO₂ scaffolds were prepared using both 200nm and 1000nm diameter colloidal PS sphere solutions. In Figure 15, shows SEM images samples prepared using 200nm spheres before (upper images) and after (lower images) the calcination steps. The polystyrene has a close packing array before the calcination step. In some areas, the packing is not perfect which lead to some cracks.

Figure 16 shows an optical image and SEM images of IO-SiO₂ scaffolds prepared using the 1000 nm PS spheres on Si. The opalescent property is readily apparent in the optical image, and the SEM images clearly show the well-ordered structure.

Figure 15, SEM images of polystyrene opals before calcination (upper 3 images) and SiO₂ inverse opals after calcination (lower 3 images) on Si wafer.

Figure 16: Optical (left) and SEM images of IO-SiO₂ scaffolds prepared using the 1000 nm PS spheres on Si.

The thicknesses of the IO-SiO₂ scaffold films were determined using stylus profilometry across features where the IO was physically scraped from the substrate. We measured a thickness of 8 μ m, indicating a 40-layered structure of the 200 nm PS spheres, and a thicknesses of 5 μ m, indicating a 5-layerd structure of the 1000 nm PS spheres.

II) Randomly Organized Scaffolds: A variety of strategies was pursued for fabricating the randomly organized scaffolds. The first was low-density silica aerogels prepared by supercritical drying of silica films made by drop casting onto glass slides and free-standing disks <1 mm in thickness. The processing of aerogels is schematically illustrated in Figure 17. Briefly, a solution (sol) is formed that is then gelled to form a silicate network. The gelled sample is subjected to solvent exchange with alcohols to make an alcogel. Since alcohols are soluble in supercritical carbon dioxide, when the alcogel is supercritically dried the solvent can be removed. The critical point of carbon dioxide is critical temperature, $T_c = 31.1$ °C and critical pressure $P_c = 1070$ psi.

In the first step, a precursor sol was prepared at 22 °C and mixed with a stir bar for 1 hour. Initially, the silica source (Silbond 40, Silbond Corporation, Weston, MI)) is hydrolyzed in the presence of ethanol with dilute hydrochloric acid (HCl). Pre-hydrolysis is necessary for subsequent gelation and network formation. After hydrolysis the silica sol was diluted to 50% v/v with 200-proof ethanol and allowed to mix with a magnetic stir

bar in a capped screw-top polypropylene centrifuge tube at ambient conditions. Separately, ammonium hydroxide (NH₄OH) base catalyst solution was prepared by mixing de-ionized water, 200 proof ethanol and 30% by weight of NH₄OH in a v/v ratio of 0.54:0.44:0.02.

To prepare the silica alcogel, 1 mL of catalyst solution was added drop wise to 10 mL of diluted hydrolyzed precursor sol with a plastic syringe. Care was taken to add the catalyst slowly (otherwise, undesirable gelling occurs producing a dense silicate material). For the films, 1 mL of the solution was dispensed on a glass substrate (microscope slide) and allowed to gel. The free-standing disks were cast in a 1-inch Petri dish for gelation. The gelation is typically completed within 10 minutes of casting the solution in both film and disk form. After gelation, the alcogel was submerged in the base catalyst solution and allowed to soak overnight in a 50/50 ethanol/water environment. Fresh ethanol was exchanged twice a day for three (3) consecutive days.

After exchanging the solvent for three (3) days as described above, the alcogels were supercritically dried with carbon dioxide (CO₂) in a Quorum Tech E3100 large-capacity supercritical dryer. The gel was placed in a mesh holder and inserted into the drying chamber. The chamber was slowly filled with liquid CO₂. Once the recorded pressure was between 850 and 950 psi, the gel was left to soak overnight. The next day the chamber was allowed to drain slowly for an hour. This enabled an effective exchange of the ethanol in the pores with CO₂ while ensuring the pressure did not drop below 800 psi. After the continuous exchange, the inlet was closed and liquid CO₂ was drained until the chamber was half-full. The temperature of the chamber was raised to 50 °C. Once the liquid CO₂ went into a supercritical phase around 1200 psi, the chamber was left to stand for one (1) hour before starting the draining process. The chamber was drained very slowly overnight. Once the pressure in the chamber dropped below 800 psi the temperature of the bath was lowered to 18 °C. The chamber was completely drained and the aerogel removed and stored in sealed containers for characterization.

The silica aerogel films and disks were characterized by measuring the thickness, light transmission in the UV and visible wavelengths (Shimadzu UV Probe 2401) and microstructure via Scanning Electron Microscope (SEM) images analyzed at PhotoMetrics Inc., Huntington Beach, CA. Optical transmission spectra for the aerogel silica films and aerogel silica disks measured in the wavelength range from 250 to 900 nm showed transmission >80% at wavelengths above 450 nm and were quite similar for films of different thicknesses (0.83 mm and 1.23 mm). Since the free-standing aerogel disks were very delicate, we measured them inside the Petri dish. Here we noted that the thinner disk (0.42 mm) showed a higher light transmission ~75% at 450 nm) than the thicker disk (0.86 mm) with a light transmission of ~60% at 450 nm. Figure 18 shows

Figure 18. Scanning electron microscope images of aerogel silica films on glass slide (Left) and aerogel disk (Right).

scanning electron microscope images for the silica aerogel films and disks. While the typical nanoscale dendritic structures are observed, the overall porosity and pore sizes are less than desired.

The second strategy explored to prepare randomly organized scaffolds is self-assembly of monodisperse SiO_2 spheres into ordered three-dimensional structures. In this project, it is critical to fabricate a high-quality colloidal crystal film with a controllable thickness. For initial and simplest approach for the fabrication, ISL is investigating the natural sedimentation of monodisperse particles under gravity. In this process, the particles in the solvent settle under gravity and self-assemble to form a film with a cubic close-packed structure, but with less order compared to the IO SiO_2 scaffolds discussed above.

Monodisperse SiO_2 spheres of varying diameters (520 nm and 960 nm) were purchased from Bangs Laboratories, Inc., Fishers, IN. and Corpuscular Inc., Cold Spring, NY. Microscope slide glasses used for the experiment were first cleaned with a solution containing 30% hydrogen peroxide and 70% sulfuric acid and then rinsed with de-ionized water and dried under a flow of dried air or nitrogen gas. The experimental procedure followed was: (1) created a 1 cm x 1 cm area using a 20 μm thick Kapton tape on the cleaned slide glass, (2) place the prepared glass substrates in a Petri dish, (3) apply a suspension (5% in de-ionized water) of the 960 nm SiO_2 particles within the 1cm x 1cm area, (4) cover the Petri dish and place on a leveled surface for *in situ* self-assembly of SiO_2 particles, (5) removing the masking tape after forming a self-assembled film. The temperature was between 20–22 $^{\circ}\text{C}$ and humidity was between 30–40% during this experiment.

The samples were evaluated for film thickness and the particle arrangement in the self-assembled film by SEM. The thickness varies between 4–21 μm within each sample. The

samples were also characterized for absorbance in the visible/NIR region with a Shimadzu UV/Vis spectrophotometer Model 2401.

The final strategy pursued for fabricating the porous scaffolds was silica xerogels. The synthesis of these materials is very similar to the low-density silica aerogels discussed above, but the relatively expensive CO₂ supercritical drying step is eliminated resulting in a denser structure. The lower density will sacrifice optical absorption for a given scaffold thickness, but may allow for more mechanically robust films at lower cost. The primary solution used to make the silica scaffold is called F-sol. F-sol consists of commercially acquired mono dispersed nanosilica particles, 40–50 nm, methylcellulose X% (MCX, where X represents weight percent of methylcellulose in the aqueous solution) and a very small amount of polyethylene glycol (PEG). The variation in the nanosilica and MCX determines the porosity of the SiO₂ network. One formulation also contained polystyrene (PS) to increase porosity.

An aqueous polymer solution was prepared by heating water at 65 °C and slowly adding MC to the polymer and prevent clumping. After all MC was uniformly dissolved, heating was stopped, and the solution mixed overnight. After de-aeration, the solution was stored for formulation with the colloidal silica.

The xerogel films were deposited onto Haynes 230 alloy substrates. First, 230 alloy substrates were sonicated in a soap solution for 10 minutes, followed by rinsing in water. Next, the substrates were sonicated in isopropanol (IPA) for 10 minutes, followed by a polishing step with 2000 grit polishing paper to roughen the surface. Finally, the substrates were rinsed off with IPA to remove any debris from the polishing. The prepared substrates were dip coated using a linear translation stage motor acquired from ThorLabs. In this arrangement, the substrate is placed in a hook like mechanism attached to the translation stage. Two speeds were used to coat the 230 substrates. The faster speed produced a thick coat on the 230 surface. Once coated the substrates were allowed to dry overnight. After the substrates were completely dry, they were fired at 600 °C for 15 minutes.

C) Infiltration of Porous Scaffolds: All of the porous scaffolds described in the previous section were infiltrated with ALD W:Al₂O₃ nanocomposite films with W cycle percentage = 33% W at a deposition temperature of 200°C. These experiments used ALD exposure times of 1-2 s and precursor partial pressures of 0.1-0.5 Torr. The purge times were 10 s. Figure 19 shows silica inverse opal (IO) deposited on a glass slide substrate (Left) and

Figure 19: Silica inverse opal (IO) deposited on glass slide (Left) and with ALD W:Al₂O₃ coatings at 33% W with a thickness of 22 nm (Center) and 44 nm (Right).

after coating with the ALD W:Al₂O₃ at 33% W with a thickness of 22 nm (Center) and 44 nm (Right). The horizontal bands visible in these images result from the solvent evaporation process used to prepare the IO, and we are working to eliminate these features to achieve uniform IO films. After 22 nm, ALD W:Al₂O₃ the IO appears blue due to optical interference effects, and after 44 nm, the IO is much darker because of the greatly increased optical absorbance of the films. For reference, the same ALD film prepared on fused silica (i.e. without the IO) appears essentially transparent.

Next, we infiltrated the self-assembled 1 μ m SiO₂ particles on glass and the SiO₂ aerogel film on glass with the 22 nm ALD W:Al₂O₃ at 33% W. Figure 20 shows the 1 μ m SiO₂ particles and SiO₂ aerogel film before coating (a, c) and after coating (b, d). It is obvious that in both cases the coated scaffolds are much darker than the surrounding glass after

Figure 20: Porous scaffolds before (a, c) and after (b, d) ALD W:Al₂O₃ coatings at 33% W with a thickness of 22 nm. Scaffolds are composed of self-assembled 1 μ m SiO₂ particles on glass substrate (a, b) and SiO₂ aerogel film cast on glass slide (c, d).

the coating, indicating at least partial infiltration of the porous scaffolds. The glass has just a single 22 nm coating, whereas the infiltrated scaffold has a much greater effective thickness due to the many coated interfaces within the film. The aerogel film (d) is darker than the particles (b) because of the much higher density of $\sim$ 10 nm voids in the aerogel as compared to the smaller number of $\sim$ 100 nm voids in the 1 μ m SiO₂ particle films. Even in the absence of any photonic enhancement, the porous scaffolds provide

enhanced optical absorption in a shorter ALD processing time for better manufacturability. This enhancement is facilitated by the excellent conformality of ALD.

We next infiltrated the SiO_2 aerogel cast disk with ALD $\text{W}:\text{Al}_2\text{O}_3$ coatings at 33% W and a thickness of 22 nm. Figure 21 shows the aerogel disk before (left) and after (right) ALD coating. The image on right is a wedge-shaped portion of the disk that was fractured after

Figure 21: SiO_2 aerogel cast disk from Fig. 20 before (left) and after (right) coating with ALD $\text{W}:\text{Al}_2\text{O}_3$ coatings at 33% W with a thickness of 22 nm. Image on right is a wedge-shaped portion of the disk that was fractured after coating to reveal that only the outer ~100 microns has been infiltrated by the ALD coating, while a majority of the aerogel remains uncoated.

Figure 22: Photographs of bare Haynes 230 substrates (a) before and (b) after coating with 20 nm $\text{W}:\text{Al}_2\text{O}_3$, 33% ALD nanocomposite, and Haynes 230 substrates coated with F SOL 0.5 PS, 4mm/s xerogel before (c) and after (d) coating with the same nanocomposite.

coating to reveal that only the outer ~100 microns has been infiltrated by the ALD coating, while a majority of the aerogel remains uncoated. These ALD coatings used ALD exposure times of 1-2 s and precursor partial pressures of 0.1-0.5 Torr. These conditions are adequate for coating planar substrates, or porous substrates with aspect ratios (ratio of pore length to pore diameter) of ~100. However, aerogel monoliths such as the SiO_2 aerogel cast disk require much longer ALD exposure times of 10 minutes and partial pressures of 10 Torr to achieve complete infiltration^{16, 40-42}. Nevertheless, even with only the outer ~100 microns coated, the sample appears completely opaque indicating that

this aerogel thickness is already more than sufficient to achieve maximum solar absorption.

Finally, we infiltrated the xerogel samples on Haynes 230 coupons with 20 nm W:Al₂O₃, 33% ALD nanocomposite. Figure 22 shows the bare Haynes 230 coupon before (a) and after (b) coating with the ALD nanocomposite. We selected the 230 coupon coated with the F SOL 0.5 PS, 4mm/s xerogel for this infiltration test. Figure 22 shows this sample before (c) and after (d) infiltration with the ALD nanocomposite. It is evident that the sample becomes nearly black after infiltration. Moreover, the sample has a matte appearance due to the rough mesostructured surface produced by the xerogel.

Figure 23 shows the optical absorption (a) and reflection (b) for the same three samples shown in Figure 19, namely the bare IO scaffold on glass, and the IO after infiltration by the ALD W:Al₂O₃ with 33% W and thicknesses of 22 and 44 nm. These data indicate that the visible light absorption is greatly increased by the ALD films, in agreement with the

visual observation. At the same time, the reflectivity is essentially unchanged in the IR region. In fact, most of the IR light is transmitted through the uncoated and coated substrates. This IR light would be reflected if the coatings were prepared on metal rather than glass, indicating that the coatings will likely have good selective absorbing properties. There are also peaks visible in both the absorption and reflection data, and the positions of these peaks shift to longer wavelengths with increasing ALD film

thickness. One way to rationalize these changes is through the simplified Bragg-Snell equation⁴³, $\lambda = 2an_{\text{eff}}$ where λ is the peak wavelength, $a = (2/3)^{1/2}d$ where d is the diameter of the spheres, and n_{eff} is the effective refractive index of the structure. As the IO becomes infiltrated with the ALD film, increases, and so the peak shifts to longer wavelengths.

Figure 24 shows the optical absorption measurements for (a) the self-assembled 1 μm SiO_2 particles on glass substrates, and (b) the SiO_2 aerogel film cast on glass slides. The blue traces show the as-prepared scaffolds and the red traces show the samples after infiltration with the ALD $\text{W}:\text{Al}_2\text{O}_3$ coatings at 33% W with a thickness of 22 nm. As expected based on the visual observations (Fig. 20), the scaffolds become much more absorbing after the ALD infiltration. The reflectance measurements (not shown) indicate that the long wavelength reflectivity is changed only very little by the ALD coating, so that most of the IR is transmitted with or without the coating. Consequently, these coated scaffolds should show good selective absorption (i.e. a high IR reflectivity) when they are prepared on metal substrates rather than on glass substrates.

Figure 25: Absorption spectrum for 10 nm $\text{W}:\text{Al}_2\text{O}_3$, 33% on xerogel-coated Haynes 230 substrate.

Figure 25 shows the absorption spectrum for the 10 nm $\text{W}:\text{Al}_2\text{O}_3$, 33% on the xerogel-coated Haynes 230 substrate shown in Fig. 22d. Using Eqns. 2-4 and the assumptions described on Pg. 14, this sample yielded a selective solar efficiency value of 0.92.

Task 1.3: Thermal Testing

A) Isothermal Testing: A collection of 7 ALD nanocomposite films on fused silica substrates of various compositions and thicknesses were subjected to 650°C in static air for 24 hours. The optical transmission (T) and reflection (R) of the nanocomposites were measured using UV-Vis-NIR spectrophotometry before and after heating, and the absorption coefficient was calculated using Eq. 1. Figure 26 shows representative absorption coefficient measurements for two ALD nanocomposite films. Figure 26a shows a 30 nm Nb:ZrO₂, 33% film as deposited (orange) and after annealing (blue). It is

obvious that the absorption coefficient in the solar region has decreased to virtually zero because of the annealing. In contrast, Figure 26b from 100 nm W:Al₂O₃, 20% shows virtually no change because of the annealing. Table 3 summarizes the results of the annealing studies where the selective solar absorber efficiencies are calculated using Eqns. 2-4 and the assumptions described in Section A. The results from Fig. 26a (30 nm

sample	metal:dielectric (m:d)	thickness (nm)	metal cycles (%)	Selective Absorber Efficiency			
				initial	after heating	change	relative change (%)
1	Nb:Al ₂ O ₃	30	33	0.9068	0.8388	-0.0680	-7.4989
2	Nb:TiO ₂	30	33	0.8985	0.0349	-0.8636	-96.1157
3	Nb:ZrO ₂	30	33	0.9082	0.0214	-0.8868	-97.6437
4	Nb:Al ₂ O ₃	100	20	0.9021	0.8354	-0.0667	-7.3939
5	Nb:ZrO ₂	100	20	0.9492	0.4013	-0.5479	-57.7223
6	W:Al ₂ O ₃	100	20	0.9128	0.9136	0.0008	0.0876
7	W:ZrO ₂	100	20	0.9402	0.6342	-0.3060	-32.5463

Table 3: Summary of annealing studies of ALD nanocomposite films. In the final column, red designates that the film has failed the isothermal anneal test, yellow is a small decrease in efficiency, and green indicates that the film has survived (passed) the isothermal anneal.

Nb:ZrO₂, 33%) are given in row 3. As expected based on the very low absorptivity after annealing, the calculated selective solar efficiency drops from 0.9082 to 0.0214 for this

film. This represents a relative change of -97.6% as presented in the final column of Table 3 indicating that this film has failed the isothermal anneal test. The results from Fig. 26b (100 nm W:Al₂O₃, 20%) are given in row 6. The selective absorber efficiency is practically unchanged for this film indicating that it has passed the isothermal anneal test. Among the 7 films in Table 3, only Sample 6 has clearly passed the test. In addition, some general trends emerge. All of the films including either ZrO₂ or TiO₂ as the dielectric failed (3, 5, 7), whereas all of the films including Al₂O₃ either passed or showed only a small change (1, 4, 6). One explanation for this difference is that both ALD ZrO₂ and TiO₂ deposit in crystalline form, and this could facilitate oxygen diffusion along grain boundaries to facilitate oxidation of the metallic nanoparticles in the film during the anneal, causing these films to become transparent. In contrast, ALD Al₂O₃ deposits in an amorphous form and so there would be no oxygen diffusion along grain boundaries. This suggests that among the dielectrics selected for this project, ALD Al₂O₃ and Nb₂O₅ should provide the best protection since both materials deposit in amorphous form.

Comparing Sample 4 (100 nm Nb:Al₂O₃, 20%) with Sample 6 (100 nm W:Al₂O₃, 20%) which are identical except for the metal, it appears that W performs better than Nb. One explanation for this difference relates to the thermodynamics of oxidation. The free energy change for Nb oxidation (-176 kcal/mol metal atoms) is more negative compared to W (-141 kcal/mol metal atoms). In other words, Nb is more easily oxidized than W. This suggests that nanocomposites with smaller free energies of oxidation will better

endure the high temperatures. Figure 27 shows a graph of the free energies of oxidation for the metals selected in this project (Co, Mo, W, Nb, Ta) as well as Ni and Cr. If the free energy is an accurate metric for oxidation resistance, then Nb and Ta should be the least resistant, W, Mo are somewhat better, and Co is the best. In addition, Ni would provide even better oxidation resistance than Co.

Several of the nanocomposite coatings on Haynes 230 alloy substrates were evaluated for adhesion using the tape test (ASTM D3359) after the 24h 650°C anneal in air and no evidence for delamination was observed.

Task 2.1. Environmental Testing

A) ALD of Thermally Robust Nanocomposite Films: This subtask is composed of two activities. The first is to prepare refractory solar selective coatings using the best-known process for environmental testing. The second activity is to improve the coating formulation to increase the high temperature tolerance from the 650°C target in Task 1.3 to the 800°C target, and to pass the barrage of environmental testing while maintaining excellent adhesion and high selective solar efficiency. At the end of Phase 1, we learned that among the metal:dielectric combinations tested, the W-Al₂O₃ was the only combination that survived a 650 °C, 24 hours (Figure 28). Therefore, moving forward, the focus was to examine what variables of the composite development have the greatest effect on the thermal stability of the film at 800°C.

Thermal Stability of W-Al₂O₃ at 800 °C

The end goal of this program is to develop a coating that is both solar selective and thermally stable at 800 °C in air. Our initial measurements used fused silica substrates rather than porous scaffolds to simplify the measurements and interpretation. These experiments focussed on the ALD film-air interactions at high temperature, and assume that these interactions are independent of the underlying substrate. The thermal stability of W-Al₂O₃ at 800 °C was tested for 100 nm of 20% W-Al₂O₃ on fused silica and shown in the blue traces in Figure 29a. As shown in Figure 29a, the 20% W-Al₂O₃ film did not retain its absorbance efficiency above 300 nm after 24 hours at 800 °C (solid blue trace is before heating, dashed blue trace is after heating). However, coating the films with a Al₂O₃ overlayer does cause the W-Al₂O₃ film to retain its absorbance (red and green traces in Fig. 29a). This suggests that the Al₂O₃ overlayer is acting as an oxygen diffusion barrier to resist oxidation of the metallic nanoparticles in the film. If we decrease the W-Al₂O₃ thickness to 55 nm, as shown in the orange traces in Figure 29b, while keeping the Al₂O₃ overlayer at 65 nm there is a slight loss in absorbance after isothermal treatment at 800 °C for 24 hours, particularly between 300-400 nm. The 100 nm 20% W-Al₂O₃ on the other hand showed a slight increase in absorbance in the same region. Increasing the W content

also negatively affects the thermal stability, as shown in the purple trace in Figure 29b. The loss in absorptivity is significant compared to that of the thinner $W-Al_2O_3$ film (orange trace Figure 29b) indicating that increasing the W content in these composite films reduces oxidation resistance of these composite films. From Figure 29, we conclude a 65 nm Al_2O_3 overlayer prevents absorptivity loss after 24 hours of isothermal treatment at 800 °C as long as the W content is 20%. However, these films did not survive an additional 24 hours (48 cumulative) at 800 °C in air.

Figure 30 illustrates the UV-Vis spectra of the $W-Al_2O_3$ films deposited on fused silica substrates with various thicknesses of Al_2O_3 overlayer versus the number of 500-800°C thermal shock cycles. Figure 30a shows the 100 nm $W-Al_2O_3$ composite coated with 33 nm of Al_2O_3 retained its absorptivity for 200 thermal cycles before a loss in absorption between 200-1000 nm is observed at 300 thermal cycles. The films turn transparent after 600 thermal cycles (Figure 30a, purple). Increasing the Al_2O_3 thickness to 65 nm further increases the number the thermal shock cycles before the films start to noticeably lose

absorptivity, only observing a drop below the as deposited absorptivity after 600 thermal cycles shown in Figure 30b. Further increasing the Al_2O_3 overlayer to 130 nm greatly

improves the composite films thermal stability, retaining absorptivity after 600 thermal cycles as shown in Figure 30c. The thermal shock cycling data from Fig. 30 is summarized in Figure 31 which shows the relative solar absorbance calculated using Equation 2 versus number of shock cycles for each of the three ALD Al_2O_3 overcoating thicknesses. It should be noted that in all cases the composite film absorptivity *increased* after the first 100-200 thermal shock cycles. The reason for this increase is not known, but closer observation of the near IR region in Figure 30 (>1000 nm) indicates an increase in IR absorptivity after initial thermal cycling. This could be due to the densification of the ALD grown Al_2O_3 throughout both the composite and protective overlayer. To examine this hypothesis, we deposited a ZrO_2 protective layer that deposits in crystalline, thus reducing the possibility of decomposition due to changes in overcoating morphology during thermal treatment. However, the ZrO_2 overcoated films did not survive isothermal treatment or 100 thermal cycles at 750°C (not shown).

Figure 31: Relative solar absorbance versus number of $500\text{--}800^\circ\text{C}$ thermal shock cycles for nm 20% W- Al_2O_3 composite coated with 33, 65, and 130 nm Al_2O_3 .

B) Synthesis of Porous Scaffolds: We examined three different type of porous scaffolds in Phase 2: silica xerogel films, spray-coated CaF_2 nanoparticle films, and spray-coated SiO_2 nanoparticle films. The solution used to make the silica xerogels (F-sol) consists of commercial mono dispersed nanosilica particles, 40–50 nm, methylcellulose (MC) and a very small amount of polyethylene glycol (PEG). The variation in the nanosilica and MC percentage determines the porosity of the SiO_2 network. The FSOL was mixed with polystyrene (PS) to increase porosity. For the PS, an aqueous PS solution was prepared by heating water at 65°C and slowly adding MC to the PS to prevent clumping. After all MC was uniformly dissolved, heating was stopped, and the solution mixed overnight. After de-aeration, the solution was stored for formulation with the colloidal silica. The xerogel films were deposited onto Haynes 230 alloy substrates. In some cases the substrates were manually roughened with 220 or 400 grit sandpaper or sand blasted prior to cleaning in order to improve adhesion. Next, the Haynes 230 alloy substrates were sonicated in a soap solution for 10 minutes, followed by rinsing in water. The substrates were then sonicated in isopropanol (IPA) for 10 minutes. The prepared substrates were dip coated using a linear translation stage motor acquired from ThorLabs. In this arrangement, the substrate is placed in a hook like mechanism attached to the translation stage. Two speeds were used, 0.25 and 0.50 mm/s. The faster speed produced a thicker coating.

The coated substrates were allowed to dry overnight and then fired at 600°C or 800°C for 15 minutes. The results of testing indicated that the coatings were too thin, and that the manual roughening was ineffective at preventing delamination. Consequently, the next batch used sand blasting, and the thicknesses were increased to be 5, 10, and 20 μm thickness.

In Q1, we performed our first IR measurements and discovered that the silica scaffolds are significantly absorbing at wavelengths longer than 4 microns. For high selective solar efficiency, our scaffold must be transparent in the IR range for blackbody radiation at $\sim 800^\circ\text{C}$, which extends to ~ 10 microns. This discovery is contrary to the spectroscopic literature on SiO_2 which has primarily focused on thin samples ($< 1 \mu\text{m}$), but is well known

in the optics literature where sample thicknesses are $> 1 \text{ mm}$. Our scaffolds are in the range 10-100 μm and this accounts for the IR absorption. This motivated us to search for alternative scaffold materials that are simultaneously transparent in the visible, transparent in the IR to ~ 10 microns, and thermally stable at 800°C in air. Metal fluorides appears to meet these requirements. For instance, Figure 32 shows the free energy of oxide formation (higher values are better for our application) and solubility in water (lower values are better) for four different metal fluoride materials with high IR transparency. Among these contenders, CaF_2 has the best combination of properties. Figure 33 shows the IR absorption spectra for CaF_2 and SiO_2 , where the 4 micron wavelength is denoted by the red dashed line for easy comparison. According to the literature, CaF_2 is stable in dry air to 1000°C but begins to degrade at 600°C in the presence of moisture. This limitation could be overcome, however, by the ALD coating that encapsulates the scaffold. We developed methods for spray coating CaF_2 micro- or nano-particles in order to assess the materials viability at an IR transparent scaffold. In addition to the CaF_2 nanoparticles, we also prepared airbrushed thin film coatings of silica nanoparticles for comparison with the silica xerogel scaffolds. All airbrushed nanoparticle thin films were applied by creating

a suspension of the nanoparticles in a 7 wt% polymethylsiloxane binding medium in xylene. Once airbrushed onto Al_2O_3 coated Haynes 230 (to improve on binding of the siloxane binder) the films were then heat-treated at 650°C for the CaF_2 nanoparticles and 800°C for SiO_2 nanoparticles for 30 minutes. The CaF_2 was treated at a lower temperature to ensure the particles were not oxidized before depositing the W- Al_2O_3 solar selective layer.

Thermal Stability of W- Al_2O_3 on High Surface Area Scaffolds

The thermal stability of the 20% W- Al_2O_3 showed promising results when protected with an overlayer of Al_2O_3 applied by ALD, so we used this strategy for ALD films deposited on high surface area scaffolds. Figure 34a shows the reflectivity UV-Vis spectrum of a Haynes 230 high temperature steel coupon (red), the same coupon coated with a silica xerogel (orange), and the same xerogel coated Haynes with 100 nm of 20% W- Al_2O_3 that was overcoated with 65 nm of Al_2O_3 (green). The xerogel itself decreased the reflectivity

between 300-1000 nm, which is attributed to changes in reflectivity of the Haynes 230 substrate during the high temperature synthesis of the xerogel. More on the changes to the Haynes 230 during thermal treatment will be addressed below, but it should be noted

that once the solar selective W-Al₂O₃ film was deposited, there is only 10% reflectivity between 300-800 nm. Examining the FTIR spectra in Figure 34b, indicates we see only a moderate decrease in reflectivity upon applying the W-Al₂O₃ between 2500 to 8000 nm. There is a significant decrease in reflectivity at wavelengths greater than 10000 nm, but this region shows only moderate overlap with the black body emissivity at 800 °C (Fig. A). More importantly, the minimal decrease in IR reflectivity between 2500-8000 nm indicates the xerogel presents a good high surface area scaffold since highest black body emission at 800 °C occurs within this wavelength region. Visibly, the xerogel coated with W-Al₂O₃ were very dark (Figure 34c). However, low porosity of the xerogel shown in Figure 34d may be the reason the scaffold reflectivity is not lower than ~10% in the visible region. A more porous scaffold would allow more effective infiltration by the ALD coating, and hence a higher optical absorption. Additionally, we also wished to examine an alternative scaffold to address the low reflectivity at 8000 nm in the IR, to further improve the films solar selective efficiency. In the pursuit of lower UV-Vis reflectivity and higher IR reflectivity, Innosense modified their silica xerogel synthesis to increase film thickness and porosity. In addition, we prepared air-brushed scaffolds of CaF₂ nanoparticles and silica nanoparticles. The scaffold synthesis, as well as the rationale for using CaF₂ will be described in detail later.

Figure 35 summarizes the reflectivity and thermal stability of solar selective coatings prepared using: (a) a more porous silica xerogel (b) airbrushed CaF₂ nanoparticles, and (c) air brushed SiO₂ nanoparticles. The porous xerogel in Figure 34 was synthesized to:

1) increase the infiltration of the W-Al₂O₃ film by ALD, thus making the films less reflective in the UV-Vis region, and 2) reduce discoloration of the underlying Haynes 230 coupon (more details will be given below). All airbrushed nanoparticles were applied by creating a suspension of the nanoparticles in a 7 wt% polymethylsiloxane binding medium in xylene. Once airbrushed onto Al₂O₃ coated Haynes 230 (to improve on binding of the siloxane binder) the films were then heat treated at 650°C for the CaF₂ nanoparticles and 800°C for SiO₂ nanoparticles for 30 minutes. The CaF₂ was treated at a lower temperature to ensure the particles were not oxidized before depositing the W-Al₂O₃ solar selective layer.

Figure 35a shows UV-Vis and FTIR reflectivity spectra of the bare xerogel (red), W-Al₂O₃ coated xerogel (orange), and the W-Al₂O₃ coated xerogel after isothermal treatment at 800°C for 24 hours (green). The modified xerogel synthesis showed similar reflectivity to those in Figure 34 when W-Al₂O₃ is applied, but once isothermally treated at 800 C in air for 24 hours, the films show a decrease in reflectivity between 300-800 nm, and an increase in IR reflectivity between 1000-8000 nm. Additionally, the xerogels showed a loss of black color and noticeable flaking after isothermal treatment (Figure 34a, right). To increase the IR reflectivity, a CaF₂ nanoparticle scaffold was used and shown in Figure 34b. The scaffold itself showed similar reflectivity in the UV-Vis region to the xerogel scaffold (Figure 34b, red) but far higher reflectivity between 8000-10000 nm. Once the W-Al₂O₃ is deposited, there is a significant decrease in reflectivity between 200-800 nm, like the xerogel, but also a noticeable decrease in reflectivity at wavelengths greater than 10000 nm. The decrease in reflectivity at 10000 nm confirms that the W-Al₂O₃ does absorb a significant amount of far IR light but, as mentioned above, this region is beyond the 800°C black body curve. After isothermally treated, CaF₂ nanoparticle films show an increase in reflectivity between 300-800 nm, and a large decrease in IR reflectivity beyond 1000 nm. Additionally, the films turned from black to dark green color (Figure 34b, right) indicating that the CaF₂ was likely oxidized. Realizing CaF₂ was susceptible to oxidation at 800°C despite the 65 nm ALD Al₂O₃ overcoating layer, a SiO₂ airbrushed nanoparticle scaffold was prepared and the ALD Al₂O₃ overcoating layer thickness was increased to 130 nm. The increased porosity of the airbrushed SiO₂ nanoparticle scaffold and greater thickness relative to the xerogel, resulted in a much higher UV-Vis absorbance (300-2500 nm) compared to that of the xerogel (Figure 34c). This also resulted in a larger decrease in IR reflectivity between 2500-8000 nm, likely due to a similar effect of the higher surface area, thickness, and porosity increasing the films IR absorbtivity. The airbrushed SiO₂ still showed an increase in reflectivity after isothermal treatment at 800°C similar to the CaF₂ and xerogels despite the thicker protective Al₂O₃ layer, but isothermal treatment at a lower temperature of 750°C (Figure 34c, blue) did not reduce the visible absorption. Additionally, the films showed no signs of flaking or loss in black color upon isothermal treatment at 750°C for 24 hours in air (Figure 34c, right).

The promising thermal stability of the Al₂O₃ protected W-Al₂O₃ shown in Figure 35c at 750°C motivated us to examine the film stability to thermal shock cycling at that temperature. Figure 36 summarizes the UV-Vis spectrum for 100 nm of 20% W-Al₂O₃ (a) coated with 33 (b), 65 (c), and 130 nm (d) of Al₂O₃ protective overlayer as the films are thermally cycles on fused silica. Figure 36a indicates the unprotected W-Al₂O₃ will not

survive thermal cycling at 750°C, but adding 33 nm Al₂O₃ overlayer increased the thermal stability for up to 100 thermal cycles, Figure 36b. Increasing the Al₂O₃ thickness to 65 nm, increases the thermal stability to 100 thermal shock cycles, but the films showed a loss in absorptivity until 200 thermal shock cycles, Figure 36c. Moreover, the films remained absorbing even after 800 thermal shock cycles. Increasing the thickness further to 130

nm, Figure 36d, showed an increase in film absorptivity after 100 thermal shock cycles, and the visible absorption remained high even after 800 thermal cycles. It should be noted that the 33 and 65 nm Al₂O₃ protected W-Al₂O₃ showed lower thermal stability towards thermal cycling compared to the same film at 800°C in Figure 35. It could be the films need to be initially heat treated to an elevated temperature to allow the densification of the ALD grown Al₂O₃ to increase the films thermal stability. It is however, important to note the significant improvement in thermal stability of the 130 nm Al₂O₃ protected 100 nm W-Al₂O₃ when thermally treating the film at 750 °C.

With the thermal stability at 750 °C shown in Figure 35c and Figure 36, we investigated the source of the significant decrease in IR reflectivity after isothermal treatment. UV-Vis and FTIR spectra of Haynes 230 coupons are shown in Figure 37. Once the bare Haynes 230 coupon (Figure 37, red) is treated at 800°C for 24 hours, there is a significant drop in reflectivity in the UV-Vis (Figure 37a) and near IR 2500-5000 nm (Figure 37b). Coating the Haynes 230 substrate with 24 nm Al₂O₃ had only a modest effect in preventing these changes after isothermal treatment at 800 °C (Figure 37a, 37b, orange). Pre-heating the at a lower temperature, 650°C for 12 hours (Figure 37, green), does decrease the

reflectivity between 300-1000 nm (Figure 37a, green) but does not affect the IR reflectivity (Figure 37b, green). It is clear that the reflectivity of the Haynes 230 decreases after exposure to high temperatures, with 800°C, including in the relevant black-body region between 2500-5000 nm, and this increases the emissivity of coated substrates. The loss in reflectivity, especially in the IR, is likely the root cause of the significant loss in IR reflectivity observed in Figure 35 after the 800 °C, 24 hour treatment.

B) In Phase 1, we measured the optical properties of the coatings using diffuse reflectance in our Cary 5000 in the range of 200-2500 nm. In order to calculate the emissivity for our coatings, we extrapolated the IR data to 10000 nm. Although this procedure yielded excellent agreement for Pyromark, where the literature emissivity had been measured over the full wavelength range, it is not possible to gauge the accuracy of the extrapolated values for our ALD coatings.

Figure 38: UV-vis (blue) and FTIR (red) reflectivity measurements performed for (a) Haynes 230 and (b) Pyromark 2500 on Haynes 230 supplied by Sandia.

To rectify this situation, we purchased and installed a Nicolet MidIR integrating sphere for our existing Nicolet 6700 FTIR spectrometer. The integrating sphere allows us to directly measure the IR reflectivity from 2000-20000 nm. Figure 38 shows the UV-Vis and FTIR measurements for two samples: (a) Haynes 230 and (b) Pyromark 2500 on Haynes 230 supplied by Sandia National Laboratory. The FTIR data for the Haynes 230 metal substrate shows a monotonically increasing reflectivity with increasing wavelength as expected for metals. The UV-Vis data shows $R=72.5\%$ at 2500 nm whereas the FTIR shows $R=64.1\%$ at this wavelength. Figure 38b shows that the reflectivity remains below $\sim 10\%$ for the Pyromark sample, and matches fairly well with previous measurements (Ho, 2014). Unlike the Haynes 230 sample, the UV-Vis and FTIR measurements match extremely well at 2500 nm. The origin for the disagreement at 2500 nm for the Haynes 230 sample is not yet understood but is under investigation.

It is instructive to compare the selective absorber efficiencies calculated from the directly measured reflectivity in the 200-20000 nm range with the values obtained by measuring the reflectivity only by UV-Vis in the 200-2500 nm range where the data was extrapolated

to 20000 nm. The green trace in Fig. 39a shows the absorptivity ($A(\lambda)=1-R(\lambda)$) measurements for the Pyromark 2500 on Haynes 230 sample performed using UV-Vis in the range of 200-2500 nm and linearly extrapolated to 10000. In contrast, Fig. 39b shows the absorptivity measured over the full range. The blue and red traces show the normalized solar and blackbody spectra, respectively, for reference. The data below each figure show the η_{sel} , α_s and ϵ values calculated from Eqns. 1-3. In general, there is good agreement between the values calculated using thee extrapolated and measured values IR reflectivities. However, $\epsilon=0.937$ is higher in Fig. 39b compared to $\epsilon=0.911$ in Fig. 39a, and this results from an under-estimation of the extrapolated IR absorption for the Pyromark sample in Fig. 39a. We next performed FTIR measurements of the silica

xerogel samples on Haynes 230 coupons that we are using as the scaffolds for the ALD infiltration. The blue and red traces in Fig. 40a show the UV-Vis and FTIR measurements, respectively. The green dashed line shows the extrapolated reflectivity that we have used previously to calculate the selective absorber efficiency. This extrapolation was based on the assumption that the silica is essentially transparent in the IR range, so that incoming radiation will reflect from the underlying Haynes 230 surface and produce a high reflectivity. It is evident in Fig. 40a that the measured reflectivity values are much lower than the extrapolated values. The origin for this discrepancy is not yet understood. Although we expect IR absorption at 9100 nm due to Si-O stretch, there are no other spectral features until 2900nm (O-H stretch). It is possible that the xerogel materials contain residual impurities from the casting and firing processes, and these impurities absorb in the infrared.

Finally, we performed FTIR reflectivity measurements of a silica aerogel on Haynes 230 substrate after infiltrating with 10 nm 30% ALD W-Al₂O₃. Figure 40b shows the data as optical absorption, and once again, there is a discontinuity at 2500 nm that we believe derives from an error in the background subtraction of the FTIR data. This sample shows high optical absorption (>95%) between 200-1000nm, and then drops monotonically between 1000-2500 nm. In phase 1, we would have extrapolated this monotonic decrease into the IR, but as shown the IR absorption actually levels off in the range 4000-7000 nm, and then increases thereafter. This behavior is due to the silica aerogel scaffold as can be seen by comparing with Fig. 40a, the spectrum for the bare scaffold. The selective solar absorption quantities calculated from Fig. 40b are: $\eta_{sel}=0.86$, $\alpha_s=0.94$ and $\epsilon=0.76$. If we linearly extrapolate the UV-Vis data into the IR instead of using the FTIR measurements, we get: $\eta_{sel}=0.87$, $\alpha_s=0.93$ and $\epsilon=0.66$.

D) Thermal Cycling: We constructed an automated thermal cycler to perform the shock temperature cycling. Figure 41a shows the instrument, which can insert and remove a quartz boat capable of holding 16 H230 coupon samples (Figure 40b). The instrument uses a motorized linear slide with 600 mm travel driven by stepper motor (Newark Instruments), an 8 channel thermocouple interface (MicroDAQ) and tube furnace (1000°C max) controlled by LabView. The instrument has been tested and has cycled coupons between 300°C and 800°C in 10 minutes. (Figure 40c). Consequently, 10,000 thermal cycles can be accomplished in ~3 months.

D) Damp Heat Test: This test measures the resistance against penetration of humidity through the coatings and is performed according to international standard IEC 62108 (test number 10.7, Procedure a). The samples were subjected to a constant climate of $85 \pm 2^\circ\text{C}$ and $85 \pm 5\%$ relative humidity. Samples were positioned in the chamber with an inclination of around 25° to the vertical, front side up. The test was carried out in a Memmert humidity chamber Model HCP108. The total testing time was 1000 hours. Twelve samples on Haynes 230 substrates were tested. All of the samples were ALD coated using 99 cycles 33% W-AlO composite ($\sim 10\text{nm}$) at 300°C , but the SiO_2 xerogel scaffold formulation was varied as described in Table 4. After performing the damp heat test, the UV-Vis and IR spectra were measured, and the adhesion was measured.

The absorbance was measured using a Perkin Elmer Lambda 1050 spectrophotometer with a 150 mm integrating sphere. The incidence angle was 8° . Measurements were performed in 5 nm steps from 280 to 2500 nm. Each sample was measured 3 times. The spectra were weighted with the ASTM G173 reference spectrum for direct radiation with AM 1.5 to compute the solar absorbance, α_s . Table 4 shows the solar absorbance α_s before and after Damp Heat testing. On average, the absorbance decreases by $\Delta\alpha_s = 0.025 \pm 0.022$ (2%). It is evident that the first set of samples (thin, low porosity) showed a 2-3x larger drop in absorbance compared to the other sets of samples.

Table 4: Solar absorptance, α_s , before and after 500 h damp heat testing

Sample	Classification	α_s <i>initial</i>	α_s after <i>damp heat</i>	Difference in α_s	Average difference in α_s	Degree of adhesion
1B	Thin, low porosity	0.951	0.929	0.022	0.053 ± 0.031	0A
1C		0.940	0.898	0.042		0A
1D		0.939	0.844	0.095		0A
2A	Thick, low porosity	0.953	0.938	0.015	0.017 ± 0.002	2A
2B		0.942	0.925	0.017		2A
2C		0.940	0.92	0.02		0A
3A	Thick, high porosity	0.959	0.947	0.012	0.013 ± 0.001	5A
3B		0.959	0.947	0.012		0A
3C		0.954	0.939	0.015		0A
4B	Thin, high porosity	0.964	0.937	0.027	0.016 ± 0.083	0A
4C		0.924	0.917	0.007		0A
4D		0.953	0.939	0.014		0A
	Average	0.948±0.011	0.923±0.027	0.025±0.022		

The adhesion was measured using (ASTM D3359), whereby the sample is X-cut and then tape-tested. In Table 4, the degree of adhesion value 0A is “removal beyond the area of the X”, 2A is “jagged removal along incisions up to 1.6mm on either side”, and 5A is “no peeling or removal”. The only correlation noted from these tests is that the 2A and 5A ratings are all in the “thick” category.

F) Neutral Salt Spray Test (NSS) ISO 9227: The NSS-test is a widely used corrosion test to simulate coastal environments. Samples are exposed to constant conditions of 35°C with a spray of a NaCl solution (50 ± 5 g/l, pH = 6.5-7.2) at 100% humidity. The samples are positioned with a tilt angle of $20 \pm 5^\circ$ respect to the vertical within the salt spray chamber. The amount of the sprayed solution is adjusted to obtain a condensation rate of 1.5 ± 0.5 ml/h on a surface of 80 cm². The condensation rates are checked at various locations within the chamber to assure of homogeneous distribution of the salt fog. A circular chamber design usually leads to higher reproducibility of test results of samples tested in different positions within the chamber.

G) UV and Humidity Test ISO 16474-3: The UV and humidity test is used to test the resistance of materials (oftentimes polymers) against alternating UV-light and humidity cycles, simulating exposure of humid environments with high radiation (e.g. Florida). The standard ISO 16474-3 replaces the previously commonly used ISO 11507. It consists of the following cycle: in the beginning, samples are exposed during 4 hours at 60 °C to UV-radiation in a specific testing chamber (see Fig. 16a). For solar absorbers the lamp type 1A (UVA-340) will be used. It emits radiation in the wavelength-range of 290-400 nm with a peak emission at 340 nm. The lamp intensity at 340 nm is 0.83W/m²/nm. The lamp

matches the solar spectrum in the wavelength range of 290-400 nm (the irradiance in this wavelength range is around 45 W/m²). Fig. 16c shows a typical spectrum of the UVA-340 lamp compared to daylight solar spectral irradiance according to CIE 85:1989. Afterwards, the samples are exposed during 4 hours at 50 °C to condensation (100 % relative humidity without irradiation). The total duration of one cycle is 8 hours. The total testing time to be performed is 1000 hours (125 cycles).

H) Coating Uniformity: A series of 5 samples was prepared using 10-20 micron thick silica xerogel films on Haynes 230 substrates, which had been abraded using 220 grit sand paper prior to deposition to improve adhesion. The samples were then coated using 100nm 20% W-Al₂O₃ and 65 nm Al₂O₃ overlayer. UV-Vis and IR measurements were performed and the absorptivity, emissivity and selective absorber efficiency were calculated using Equations 1-3. The results are given in Table 5, and demonstrates that the variation in efficiency among the duplicate samples is only 2%.

Sample ID	Absorbance (%)	Emission (%)	Efficiency (%)
620-9	86.3	58.2	80.3
620-10	84.0	55.6	78.2
620-11	84.8	58.2	78.9
623-1	80.7	46.0	76.0
623-2	81.4	47.3	76.6
Average	83.4	53.1	78.0
Std Dev	2.1	5.3	1.6
Std Dev (%)	2.5	10.1	2.0

Table 5: Absorbance, emission, and efficiency for duplicate set of coatings.

Task 2.2: Long Term Isothermal Testing

A series of 3 samples was prepared using 5, 10, and 20 micron thick silica xerogel films on Haynes 230 substrates, which had been abraded using 220 grit sand paper prior to deposition to improve adhesion. The samples were then coated using 100nm 20% W-Al₂O₃ and 65 nm Al₂O₃ overlayer. UV-Vis and IR spectra were recorded prior to heating. These samples are currently undergoing long-term isothermal testing.

Task 2.3: Commercialization Plan Development

A) Calculate LCOC for Coatings: The levelized cost of coating (LCOC) will be computed according to the method proposed by C. Ho and J. Pacheco. The LCOC are defined as the fraction of annualized coating cost and the annual thermal yield.

$$LCOC = \frac{C_{annual}}{E_{thermal}}$$

The annualized coating costs include annualized initial coating costs, annualized costs for recoating and annualized costs for the necessary additional or fewer heliostats compared to a reference case.

$$C_{\text{annual}} = C_{\text{an,coating init}} + C_{\text{an,recoating}} + C_{\text{an,heliostat}}$$

$$C_{\text{an,coating init}} = \frac{c_{\text{initial coating costs}} (\$/\text{m}^2) \cdot A_{\text{receiver}} (\text{m}^2)}{\text{Lifetime plant (yrs)}}$$

$$C_{\text{an,recoating}} = \frac{c_{\text{recoating}} (\$/\text{m}^2) \cdot A_{\text{receiver}} (\text{m}^2)}{\text{recoating interval (yrs)}}$$

$$C_{\text{an,heliostat}} = \frac{A_{\text{additional or fewer heliostats}} (\text{m}^2) \cdot c_{\text{heliostat}} (\$/\text{m}^2)}{\text{Lifetime plant (yrs)}}$$

The thermal yield is defined as the thermal yield after fresh application of the coating minus the losses due to degradation of the coating and the losses caused by downtime for reapplication of the coating.

$$E_{\text{thermal}} = E_{\text{th,new}} - E_{\text{th,degradation}} - E_{\text{th,downtime}}$$

A stepwise rank regression analysis carried out by C. Ho showed that both the value of the solar absorptance and the thermal emittance are the most significant parameters when computing the LCOC. For this reason, the thermo-optical efficiency of the receiver will be computed using a thermal FEM receiver model, which is coupled to a raytracer model. So far, the model only considers a single value for the solar absorptance (gray body radiation) for the computation of the absorbed solar radiation and a second single value for the thermal emittance (gray body radiation) for the computation of the losses by IR radiation. Therefore, the model will be enhanced to also consider spectral properties of the coatings on the absorber tubes of the receiver.

In order to obtain the number of additional or fewer heliostats a reference system has to be defined. Using this reference system, the different annual thermal yields can be computed using the method described in the following figure. In a first step, a receiver thermal efficiency curve will be computed using DLR's detailed thermo-optical ASTRID model. Based on the receiver efficiency curves the number of necessary heliostats can be defined and finally the annual thermal energy production can be computed based on weather data.

The defined approach produces the following subtasks and dependencies.

The work has been started at DLR according to this plan. The following sections describe the work performed in the first two quarters of 2017:

The reference system

The used reference system should adhere to the following two criteria:

1. Produce a commercially relevant temperature- and flux profile on the absorber tubes of the receiver
2. All necessary data on the system has to be publicly available in order to allow comparison of other coating developments

The “Crescent dunes” power plant (USA) fulfils the requirement of a commercially relevant temperature- and flux profile on the absorber tubes, because it is a commercial system. Furthermore, DLR has collected all publicly available data on the Crescent Dunes system and has set up a specification sheet. The necessary data points, which are not available, can be estimated without dramatically changing the characteristics of the Crescent Dunes system. The main missing data are the positions of the heliostats in the heliostat field. For this reason, an equivalent heliostat field has been deduced. For this purpose, the geo-position (Latitude and Longitude) of approximately 600 heliostats and the tower was measured using Google Earth. Each measured heliostat was assigned the corresponding ring number in the heliostat field and a correlation between ring number and ring radius was deduced. (see figure below on the left) Further, on the Azimuth step as a function of the ring radius was deduced. The azimuthal distance follows the real example whilst neglecting extra roads or transmission lines.

The following pictures show the resulting heliostat positions (red) over a screenshot from Google Maps of the Crescent Dunes plant.

Figure 42: Crescent Dunes heliostat field (Google maps) and reproduced equivalent heliostat field

Implementation of spectral absorptance into raytracing software

The consideration of the spectral absorptance has been implemented into the raytracing software SPRAY. The raytracing model has been validated using an analytical model based on View factors and Gebhart factors for two simplified cases:

1. flat plate
2. two absorber tubes

In the flat plate case, a flat plate is irradiated by parallel solar radiation (ASTM-G173). The irradiated surface of the plate has a spectral hemispherical absorptance of the type $\alpha = f(\lambda)$.

Figure. 43 - flat plate

The total absorbed power computed by the raytracer can be directly compared to the analytically computed absorbed power $\dot{q}_{absorbed,total}$:

$$\dot{q}_{absorbed,total} = \alpha_s \cdot \dot{q}_{sol}$$

With:

$$\alpha_s = \frac{\int_0^\infty \alpha(\lambda) \cdot G(\lambda) d\lambda}{\int_0^\infty G(\lambda) d\lambda}$$

Where $\alpha(\lambda)$ is the spectral absorptance and $G(\lambda)$ is the solar emission ASTM G173-03 Reference spectrum (AM1.5). For the flat plate case, the analytical model and the raytracing model agree. In a second step, the raytracer model is validated with the following example:

1. Two “infinitely”¹ long parallel tubes, directly placed next to each other (no gap)
2. Parallel incident solar radiation (ASTM-G173) (as shown on following figure)
3. the surface of the tubes has a spectral hemispherical absorptance of the type $\alpha = f(\lambda)$

The analytical model is based on View Factors and Gebhart Factors⁴⁴. The View Factor calculation has been validated by comparison with the View Factors computed by ANSYS for the same model. The following graph shows the deviation between the analytical and the raytracer model for three different levels of detail of the analytical model: (the raytracer model always considers multiple reflections)

1. no consideration of reflection
2. only consideration of the first reflection
3. consideration of multiple reflection

It can be seen that for the highest deviations are found for the tube surface 6 and 7 for the “no reflection” case, as the cavity effect at these surfaces is the highest. This deviation disappears below the expected values of the variation coefficient for the raytracing simulation if multiple reflections are considered by the analytical model.

Figure. 44 - Results validation of raytracer model

Setup of receiver model in FEM

The receiver configuration has been deduced from the collected information of the original Crescent Dunes system (see appendix). A thermal FEM model of the Crescent Dunes receiver has been set up in ANSYS. This model considers both the back wall insulation and the absorber tubes of the receiver. Effectively, the code automatically generates the complete FEM geometry and mesh based. Its interface to a raytracing software allows to compute a realistic heat flux distributions on the absorber surface for a given heliostat

¹ The ratio between evaluated section and modeled section is reduced as long as end effects do not influence the results anymore

field, time point and location of the solar power plant. Hence, the model accounts for both blocking and reflection losses of the solar radiation on all modeled components of the receiver. The headers are neglected as they are generally insulated and thereby do not participate in the conversion of solar radiation. The heat transfer to the fluid is modeled using one-dimensional fluid flow elements allowing mass and heat transportation. The local heat transfer coefficients are computed based on Nusselt correlations as a function of the local fluid temperature and Reynolds number. The thermal radiative exchange between the absorber tubes and the insulation as well as the radiation to the ambient is modeled using the radiosity Method⁴⁵. Only natural convection losses is considered. These losses are modeled by a global heat transfer coefficients issued from⁴⁶. A mass flow control algorithm adapts the mass flow iteratively for each flow path through the receiver in order to get the desired outlet temperature for different load scenarios.

Figure. 45 - Working principle ASTRID model

In order to compare the different coatings in terms of receiver efficiency it is assumed that the receiver geometry and panel interconnection are kept constant for all coating types. In addition, the local maximum allowable flux density will be kept constant for all considered coatings.⁴⁷ The Aiming points on the receiver are attributed according to the simplified model described in⁴⁸. The following picture shows the resulting solar flux for the computed aiming parameters at the design point of the receiver (21.03. at 12:00) for the allowable flux densities expected for Pyromark.

Influence of number of heliostats on the annual field efficiency

To determine the influence of heliostat field size on the heliostat field efficiency variations of a heliostat field based on Crescent Dunes was made. The same heliostat dimensions, tower size, receiver power and number of heliostats was used as a reference. An estimation of the receiver efficiency and the heliostat beam quality was made. For a fixed number of heliostats, the field layout was optimized by minimizing the annual LCOH (levelized cost of heat) of the solar field using HFLCAL software. As shown in Fig. 46, a

linear correlation can be used to guess the heliostat field efficiency of an optimized field layout as a good estimation in the relevant range of heliostat field sizes.

Figure 46: Heliostat field efficiency with varying field size

Conclusions: The key results from our project are as follows:

- 1) Our DOE study revealed that the metal content is the critical parameter controlling spectral selectivity. In contrast, the nanocomposite film thickness and metal:dielectric pair are not significant for the spectral selectivity of the ALD nanocomposite films. Therefore, we are justified in modeling the optical constants for the nanocomposite films using an EMA model based on measured optical constants for the pure metal and dielectric components.
- 2) The aerogel, IO, self-assembly, and xerogel strategies all produce porous scaffolds that yield optically dense films after infiltration with the ALD nanocomposite films. Among these, IO will be pursued further since the well-ordered structures are easily compared with theory, and xerogels will be continued as this is best suited for scale-up.
- 3) We developed a computer model based on finite difference time domain (FDTD) suitable for simulating photonic scaffolds with arbitrary structure and composition. This model takes as input optical constants obtained by fitting spectroscopic ellipsometric measurements of the ALD nanocomposites. This model reproduces measured reflectivity curves to ~10% accuracy.
- 4) Thermal testing has identified nanocomposite formulations that survive high temperatures in air. In addition, metals with low free energies of oxidation coupled with amorphous dielectrics might yield the most robust nanocomposites.
- 5) By adjusting the metal content of the ALD nanocomposite films, and by using an ALD Al_2O_3 overcoating layer, we have created materials that withstand 24 hours and 600 thermal shock cycles at 800°C in air.
- 6) Silica scaffolds show a relatively strong absorbance at wavelengths above 4000 nm, and this overlaps significantly with the black body radiation curve. In contrast, calcium fluoride scaffolds are transparent to 7000 nm, but they must be encapsulated by ALD layers to prevent oxidation at 800°C in air.
- 7) The spectral selectivity of our refractory solar selective coatings relies on the underlying metal substrate (e.g. the Haynes 230) to act as an IR reflecting mirror because both the scaffold and the ALD films are transparent in the IR. Although this scheme works well at lower temperatures, upon 800°C anneal the Haynes 230 substrate oxidizes and the IR reflectivity diminishes. It is possible that a different metal alloy substrate or a thicker coating might eliminate this problem.
- 8) We have developed an improved model for LCOC calculations using ray tracing and finite element modeling that includes spectral properties of the coatings on the absorber tubes of the receiver.

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