PROGRESS IN DEVELOPMENT OF HIGH-TEMPERATURE SOLAR-SELECTIVE COATING

C.E. Kennedy
National Renewable Energy Laboratory (NREL),
1617 Cole Blvd., MS-3321, Golden, CO 80401-3393, 303-384-6272, 303-384-6103 (fax),
cheryl_kennedy@nrel.gov

H. Price
National Renewable Energy Laboratory (NREL),
1617 Cole Blvd., MS-1725, Golden, CO 80401-3393, 303-384-7437, 303-384-7595 (fax),
hank_price@nrel.gov

ABSTRACT

Improving the properties of the selective coating on the receiver represents one of the best opportunities for improving the efficiency of parabolic trough collectors and reducing the cost of solar electricity. Additionally, increasing the operating temperature above the current operating limits of 400°C can improve power cycle efficiency and reduce the cost of thermal energy storage resulting in reductions in the cost of solar electricity. Current coatings do not have the stability and performance necessary to move to higher operating temperatures. The objective of this effort was to develop new, more-efficient selective coatings with both high solar absorptance (\(\alpha \geq 0.96\)) and low thermal emittance (\(\varepsilon \leq 0.07\) at 400°C) that are thermally stable above 500°C, ideally in air, with improved durability and manufacturability and reduced cost. Using computer-aided design software, we successfully modeled a solar-selective coating composed of materials stable at high temperature that exceeded our property goals. In preparation for characterization of samples of these new coatings, a round-robin experiment was conducted to verify the accuracy of the selective coating reflectance measurements.

Key words: absorbers, high-temperature, parabolic trough, solar-selective coating

1.0 INTRODUCTION

Improving the properties of the selective coating on the receiver and increasing the solar field operating temperature to >400°C can improve the overall solar to electric efficiency of parabolic trough solar power plant and reduce the cost of solar electricity. To accomplish this, new, more-efficient selective coatings are needed that have both high solar absorptance and low thermal emittance at elevated temperatures. Although designs are likely to use coatings in evacuated environments, the coatings need to be stable in air in case the vacuum is breached. Current coatings do not have the stability and performance desired for moving to higher operating temperatures. For efficient photothermal conversion, solar absorber surfaces must have low reflectance (\(\rho \approx 0\)) at wavelengths (\(\lambda\)) \(\leq 2\) \(\mu\)m and a high reflectance (\(\rho \approx 1\)) at \(\lambda \geq 2\) \(\mu\)m. The cutoff may be higher or lower depending on the operating temperature. For parabolic trough applications, the spectrally selective surface should be thermally stable above 500°C, ideally in air, and have a solar absorptance greater than 0.96 and a thermal emittance below 0.07 at 400°C. Achieving the improved properties is very important if the parabolic troughs are going to move to higher temperatures.

Figure 1 shows the influence that receiver technology can have on the cost of electricity. Assuming a solar field working temperature of 400°C, the relative cost of electricity for current receiver selective coatings decreases with improvements in the optical properties; moving from the original Luz black chrome

![Graph showing the influence of receiver technology on cost of electricity.](image)

**Fig. 1. Influence of receiver technology on cost of electricity.**

(DOE parabolic trough 2005 reference power plant configuration, 100 MWe solar only SEGS, 6-hours of thermal energy storage)
to the Luz cermet to the newer generation receivers from Solel and Schott. The figure also shows the reduction in the cost of electricity that could be achieved by reaching the DOE goals. The Solel UVAC as tested results represents the DOE baseline technology assumption for near-term future parabolic trough plants. The DOE long-term goal represents a 10% improvement in the cost of electricity. The uncertainty in the values shown in Figure 1 have not been carefully quantified at this point, but are thought to be on the order of several percent of the values shown.

Experience from the Solar Energy Generating Systems (SEGS) plants has shown that the reliability and lifetime of the parabolic trough collector receiver tube or heat-collection element (HCE) is the most significant O&M issue for existing and future parabolic trough plants. HCE designs use an evacuated receiver fabricated from stainless-steel tubing with a cermet coating (cermets are highly absorbing metal-dielectric composites consisting of fine metal particles in a dielectric or ceramic matrix), a Pyrex® glass envelope coated with an antireflection (AR) coating, and a conventional glass-to-metal seal. The original HCE design used a Mo-Al₂O₃ cermet solar coating deposited by radiofrequency (RF) planar sputtering has shown good optical properties of α = 0.96 and εₐₐₚₖₜ₇₃₀ = 0.16 (where εₐₐₚₖₜ₇₃₀ is the ε measured at 350°C) for 350°C < T < 500°C in vacuum [1]. Although the Mo-Al₂O₃ cermet coating has demonstrated good thermal performance in evacuated HCE configurations, it has exhibited limited durability when exposed to air at parabolic trough operating temperatures. When the vacuum tube is compromised, after exposure to air at operating temperatures above 300°C, the Mo-Al₂O₃ cermet degrades and coats the glass tube with an opaque white precipitate that gives the tube the appearance of a fluorescent light. This rapid degradation of the cermet absorber coating significantly impacts solar field performance. Air leakage at the glass-to-metal seal appears to be the primary cause of failure, resulting in a loss of vacuum and oxygen exposure of the cermet coating. Historically, HCE failure rates were approximately 3%–4%/year [2].

The original receiver supplier of the SEGS plants, Luz Industries Israel, went out of business in 1991. Subsequently Solel Solar Systems purchased the Luz receiver technology and manufacturing facility. Solel continued to develop the receiver technology and has been providing spare receivers to several of the existing facilities. Solel has developed a new HCE product—an improved receiver tube called the Universal Vacuum Collector (UVAC). The UVAC uses a new multilayer Al₂O₃-based cermet that does not use Mo, with an improved AR coating and is quoted to have absorptance of 96% and emittance of 0.10 at 400°C, and to be stable in air and humidity at high temperatures [3]. Field-testing of the performance and durability of the UVAC receivers at existing plants has shown significantly improved reliability and performance compared to the original receivers. Laboratory tests of selective coating properties have not been quite as good as the manufacturer’s specification. Figure 1 shows how the difference in the as-tested properties (t) compare to the manufactures specified properties (s). It should be noted that the tested properties are from the first generation UVAC. Solel has continued to improve the UVAC design and likely the selective coating properties in subsequent generations of UVAC tubes. Some degradation of the selective coating has been observed in receivers that have lost vacuum.

Until recently, Solel Solar Systems, Ltd., manufactured the only commercially available replacement HCE. Schott recently began producing a replacement receiver as well. The Schott receiver uses a selective coating similar to the original Luz Mo-Al₂O₃ cermet. Schott has developed a more robust glass to metal seal design in an effort to preclude exposure to air and the fluorescing failure experience of the original Luz cermet receivers. The Schott receivers are also being field tested at this point, and also show improved performance and excellent reliability (zero failures after 1-year in service).

At this point, none of the existing coatings have proven to be stable in air at 400°C. Achieving our goal for a solar-selective coating that is stable in air at temperatures greater than 400°C requires high thermal and structural stabilities for both the combined and individual layers, excellent adhesion between the substrate and the adjacent layers, suitable texture to drive the nucleation and subsequent growth of layers with suitable morphology, enhanced resistance to thermal and mechanical stresses, and acceptable thermal and electrical conductivities. Good continuity and conformability over the tube, as well as compatibility with fabrication techniques, are also desirable. The material should have a low diffusion coefficient at high temperature and be stable with respect to chemical interactions with the oxidation product, including any secondary phases present, over long periods of time over elevated temperature. Selecting materials with elevated melting points and large negative free energies of formation can meet these objectives. Materials that form multicomponent oxide scale with a low vapor pressure composed of a refractory oxide skeleton and an amorphous (glass) oxide component provide good oxidation performance. Modifying the chemical composition of the oxide surface layer to decrease inward diffusion of oxygen can control the oxidation resistance of non-oxide ceramics. Stable nanocrystalline or amorphous materials are the most desirable (and practical) for diffusion barrier applications, especially in light of material and process limitations. As grain size is decreased, hardness, wear resistance, and strength increase. Higher-conductivity materials have improved thermal shock resistance, and thermal-stress failures are reduced for materials that possess some ductility at room temperature. High thermal stability is manifested by high melting points, single-compound formation, and lack of phase transformations at elevated temperature.

To identify potential high-temperature absorbers, we have reviewed the literature for medium- to high-temperature absorber coatings [4]. Several materials have the appropriate optical properties and should be durable at operating temperatures above 500°C. The dependence of diffusion processes on the melting temperature makes it desirable to select materials with a high melting point. Accordingly,
refractory metallic systems with characteristically high melting point and chemical inertness serve as viable candidates for selective coatings. Various transition metals—particularly those formed from the refractory metals of groups IV A, VA, and VI A and their binary and ternary compounds—have been suggested for high-temperature applications [5]. The titanium, zirconium, or hafnium metal boride, carbide, oxide, nitride, and silicide materials have some of the highest melting points in nature, with HfC having the highest melting point at 3316°C. These materials also have a high degree of spectral selectivity, high hardness, and improved wear, corrosion, and oxidation resistance [6,7]. A double-cermet film structure has been developed that has higher photothermal conversion efficiency than surfaces using a homogeneous cermet layer or a graded film structure [8]. Combining several concepts, a high-temperature solar-selective coating could be developed made from materials with intrinsic solar selectivity and high-temperature stability using multiple cermet layers, along with appropriate surface texturing and incorporating multiple AR coatings.

The optical properties of the refractory metal compounds have a high degree of flexibility; with further research, multiple-layer cerments with noble metals could be viable high-temperature absorbers for the Concentrating Solar Power (CSP) program. To achieve our goals, we proposed the following:

- Development of high-temperature solar-selective coatings using multiple cermet layers by physical vapor deposition (PVD)
- Material characterization, high-temperature optical characterization, and durability testing to verify functionality.

### 2.0 HIGH-TEMPERATURE SOLAR-SELECTIVE COATING DEVELOPMENT

#### 2.1 Optical Modeling

Solar-selective coatings made with multiple cermet layers of refractory metal compounds that incorporate surface texturing and multiple AR layers are likely to be successful and meet the CSP optical and durability requirements. As a first step, Essential Macleod™ [9] was used to optically model solar-selective designs or refine existing ones and extract optical constants of the steel substrate used in the design. The software allowed the identification and selection of the coating thickness and composition required to deposit the most-promising candidates.

We modeled multilayer coatings because they were significantly easier to model than cerments, with the expectation of later converting the best multilayer design into a cermet and reviewed the material properties of candidate materials for the solar-selective coating design. Materials with low thermal stability and high reactivity were down-selected, and materials with more suitable properties were modeled. For example, based on their melting points, the metals W, Mo, Ir, Os, and Ta are prime candidates for high-temperature applications; but W, Mo, Os, and Ta have very poor oxidation resistance and molybdenum oxide is very volatile. The original concept did not work as well as hoped (NREL#1), but we found a low-emittance, high-temperature material that, when modeled, gave solar-selective coatings with excellent emittance; however, the absorptance of modeled coatings was lower than desired (NREL#2). The addition of an AR layer composed of very thin (quarter-wave) dielectric material improved the absorptance (NREL#3). AR coatings are also made from multiple quarter-wave layers of two materials with high and low indices of refraction to create the required properties. As shown in Table

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Measured Existing Materials</th>
<th>NREL’s Modeled Prototype Absorber</th>
<th>Further Refinement of NREL’s Modeled Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Black Chrome</td>
<td>Luz Cermet</td>
<td>UVAC</td>
</tr>
<tr>
<td>Solar α</td>
<td>0.916</td>
<td>0.938</td>
<td>0.954</td>
</tr>
<tr>
<td>Thermal ε @</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>0.081</td>
<td>0.061</td>
<td>0.052</td>
</tr>
<tr>
<td>100°C</td>
<td>0.109</td>
<td>0.077</td>
<td>0.067</td>
</tr>
<tr>
<td>200°C</td>
<td>0.146</td>
<td>0.095</td>
<td>0.085</td>
</tr>
<tr>
<td>300°C</td>
<td>0.183</td>
<td>0.118</td>
<td>0.107</td>
</tr>
<tr>
<td>400°C</td>
<td>0.220</td>
<td>0.146</td>
<td>0.134</td>
</tr>
<tr>
<td>450°C</td>
<td>0.239</td>
<td>0.162</td>
<td>0.149</td>
</tr>
<tr>
<td>500°C</td>
<td>0.257</td>
<td>0.179</td>
<td>0.165</td>
</tr>
</tbody>
</table>
1, additional AR layers further improved the absorptance, but increased the complexity of the design (NREL#4). The difference between the A and B models is a material substitution in one of the layers. The A material has the advantage of raising the absorption, but the disadvantage of also slightly raising the emittance. As shown in Table 1, with further refinement, we were able to both improve the absorptance and significantly reduce the number of layers in the design (NREL#5) to a construction that is significantly easier to deposit. Finer refinements of the AR layers with a more data points modeled between 300 and 500 nm resulted in a = 0.959 and e = 0.061 at 400°C for the multilayer stack (NREL#6A). All of the modeled designs had lower predicted radiation losses than the existing coatings. Figure 2 shows the predicted radiation loss (per square meter of collector aperture) for receivers on a Luz LS-2 collector. The NREL#6A coating exceeds the DOE selective coating property goals by about 1% overall because 1% in emittance is about equivalent to 1.2% in absorptance. NREL is pursuing the intellectual property of the modeled coatings. There is significant uncertainty in the real property values of the modeled selective coatings and the key issue becomes trying to make the coating and testing its actual properties. Incorporating improved AR coatings, cermets, and texturing the surface should further improve the solar-selective coating; however, trade-offs exist between simultaneously obtaining both low emittance and high absorptance.

![Graph showing thermal losses vs. surface temperature](image)

**Fig. 2.** Predicted receiver radiation losses for existing selective coatings and new NREL modeled coating.

### 2.2 Deposition

Deposited solar-selective coatings that reproduce the modeled coatings are likely to be successful and meet the CSP optical and durability requirements. To start the solar-selective prototyping, we elected to use the ion-assisted electron-beam (e-beam) chamber in the NREL multi-chamber vacuum system because of the versatility and lower cost for initial material prototyping. The e-beam gun uses 7-cc crucibles to deposit six materials sequentially and can co-deposit two different materials simultaneously. Dielectrics can be evaporated directly, and an ion gun can be used to improve the quality, composition, and density of the coating. By controlling the deposition parameters, the microstructure of the coatings can be deposited from porous to columnar to amorphous, and with co-deposition, a cermet can be made where the dielectric is filled with the metal. The dielectric chemistry can be modified by the introduction of gases (e.g., O₂, N₂, CO₂) into the deposition process, called activated reactive evaporation (ARE), resulting in materials with widely different material properties. We have a great deal of flexibility in the materials we can prototype for the high-temperature solar-selective coatings. Initially, our substrate is glass because glass is readily available and lower in cost than the eventual polished stainless steel. In addition, it is transparent, allowing the extraction of the refractive indices of the coatings from the reflectance and transmittance data with the Essential Macleod™ software. Eventually, the prototype solar-selective coating will be deposited on a polished stainless-steel substrate suitable to continued use at high temperatures.

AR coatings are typically one-quarter-wavelength stacks of dielectrics of alternating high and low refractive indices. Layer thickness control is therefore critical to the optical properties. Deposition parameters are critical to the microstructure, which defines the mechanical and thermal properties. A crude selective coating could be made at this time, but without careful control of the thickness and deposition parameters, there would be little expectation that the coating would match either the requirements or model. Accordingly, we are calibrating materials and thickness-monitoring equipment; checking the η and κ values; verifying the thickness and uniformity; and checking optical properties, stoichiometry, and morphology of the individual layers for the NREL#6A and 6B architecture. In addition, a pneumatic shutter allowing careful control of the critical layer thicknesses must be installed and wired to the thin-film controller. After we have completed characterization of the individual layers, we will deposit the modeled architectures, compare the measured properties with the model, and make further refinements to the model and coating deposition.

### 3.0 CHARACTERIZATION AND DURABILITY TESTING TO VERIFY FUNCTIONALITY

#### 3.1 Round-Robin Testing

Development of spectrally selective materials also depends on reliable characterization of their composition, morphology, physical, and optical properties. The key for high-temperature usage is low ε. Emittance is frequently reported based on fitting reflectance data over the thermal spectrum to blackbody curves. This approach has the potential to lead to unrealistic predictions of high efficiencies at high temperatures because emittances are systematically underestimated [10]. Furthermore, selective coatings can degrade at high temperatures due to thermal load, high humidity or water condensation on the absorber surface, atmospheric corrosion, diffusion processes, chemical reactions, and poor interlayer adhesion [11]. It is important that calculated data are verified with emittance measurements conducted at high temperature before using high-temperature emittance calculated from room-
We needed to develop the protocols for testing the thermal/optic properties of selective coating, verify and document that the reflectance measurements are accurate, and ensure that the low-temperature measurements are consistent with the high-temperature measurements. To do so, we conducted a round-robin experiment with four laboratories with infrared (IR) reflectance and high-temperature capabilities—NREL’s FTIR laboratory, Sandia National Laboratories (SNL), AZTechnologies (AZT), and Surface Optics Corporation (SOC). AZT, NREL, and SOC measured two UVAC samples (A and B), a Luz Cermet sample, and a Black Ni (Black Ni was excluded at SOC because of cost) at room temperature, where each tube sample was cut into four 90-degree sections and measurements were taken on each 90-degree section (referred to as samples a, b, c, and d). SOC measured UVAC A samples at incident angles of 15º, 30º, 45º, and 60º at room temperature from 0.3 µm to 26 µm. NREL and SOC also made measurements on UVAC A samples from 1.5 µm to 26 µm at 200ºC, 400ºC, and again, at room temperature after being heated. SNL needs to measure all the samples from 1.5 µm to 26 µm at room temperature and the UVAC A from 1.5 µm to 26 µm at 200ºC, 400ºC, and again, at room temperature after being heated. Figures 3 and 4 summarize some of the AZT data received. For comparison, the SOC data are compared to the earlier AZT measurements provided by SNL (Fig. 5). Still to be completed are the following: correlating the geometry corrections; comparing the AZT, NREL, SOC, and SNL (when received) data; comparing the high-temperature measurements with the blackbody calculations; comparing incident angle with near-normal measurements; and reporting the results.

### 3.2 Thermal Stability

An important requirement for the absorber coatings is long-term thermal stability above 400ºC, ideally in air. Thermal stability is sometimes based on the thermal properties of the individual materials or the processing temperature parameters, and actual durability data are rarely known for high-temperature absorber coatings. At high temperatures, thermal emittance is the dominant source of losses, and the requirement of low emittance often leads to complex designs that are frequently susceptible to degradation at the working temperature. Compared to the desired lifetime (5–30 years), durability or thermal stability is typically tested by heating the selective coating—typically in a vacuum oven, but sometimes in air—for a relatively short duration (hundreds of hours).

To determine the durability and thermal stability of the spectrally selective coatings being developed, a high-temperature inert-gas oven was purchased and installed that will allow the coatings to be exposed at their operating temperatures and conditions for longer periods of time. The BlueM IGF-6680-E-MP550 oven has a temperature range of +1100ºF (+593ºC) in an inert-gas environment (N₂, Ar, CO₂, He, and forming gas [a mixture of H₂ and N₂]). The oven has a temperature data for each selective coating; but it is more important that we make sure the reflectance measurements are accurate in the first place.
NIST traceable certificate of calibration. It has data acquisition software to allow the operator to configure, control, and log data, to write and store programs (profiles) on a computer, and provides trending charts, bar graphs, and additional graphical displays.

International Energy Agency (IEA) Task X has a performance criterion (PC) developed for flat-plate collector selective absorber testing (i.e., non-concentrating, 1–2X sunlight intensity) [12]. The PC describes the influence in the change of solar absorption (Δαs) and emittance (Δε) on the solar fraction:

$$PC = -\Delta \alpha_s + 0.25 \cdot \Delta \varepsilon \leq 0.05,$$

assuming a service lifetime of at least 25 years and a decrease in the annual solar fraction of 5%. Service lifetime testing for this criterion is performed by exposing the absorber coatings for 200 h at 250°C. If the material survives, it is then exposed for 75 h at 300°C, followed by 600 h at 40°C/95% relative humidity (RH), then 85 h at 60°C/95%RH. After exposure testing, the emittance is typically measured at 100°C. No similar criterion has been developed for testing the service lifetime of high-temperature absorbers for CSP applications. By testing commercial and prototype solar-selective samples for longer periods of time at higher temperatures in the new oven, the durability of the materials can be estimated, and it is anticipated that a suitable criterion can be developed for high-temperature selective surfaces applicable for concentrating applications.

4.0 CONCLUSIONS AND NEXT STEPS

Using computer-aided design software, we have successfully modeled optically a solar-selective coating with α = 0.959 and ε = 0.061 at 400°C composed of materials stable at high temperature. This exceeds the goal specification by about 1% overall, because 1% in emittance is equivalent to about 1.2% in absorbance. Producing the modeled coating prototype is now imperative.

Further modeling refinements and the effect of errors during deposition will be investigated with the software. The entire HCE (air/glass/AR coating, vacuum, AR coating/solar-selective coating/stainless steel) structure will also be modeled. We will also be measuring the optical properties of the deposited film layers, extracting the optical constants, and applying the constants to the model. Converting from a multilayer to a cermet and incorporating texturing will follow. Improvements are expected by incorporating improved AR coatings, cermets, and textured surfaces; however, trade-offs exist between low emittance and high absorbance.

Still to be done are the following activities: complete the calibration of materials and thickness monitoring equipment; check the n and k values; verify the thickness and uniformity; and check optical properties, stoichiometry, and morphology of the individual layers. In addition, a pneumatic shutter will be installed and wired to the thin-film controller, allowing careful control of the critical layer thicknesses. After the individual layers have been characterized, we will deposit the modeled structure, compare the measured properties with the model, and make further refinements to the model and coating deposition. We may try methods to create surface texture.

In thin-film deposition, a good general rule of thumb is that the lower the process pressure and the more energetic the process, the more control exists over the film properties, but the higher the cost of the equipment and the coating. Physical vapor deposition (PVD) techniques were elected to give greater control over the film properties. It is the intention that after a viable high-temperature solar-selective coating is developed, the feasibility of lower-cost methods will be explored and coating industry experts will perform a rigorous cost analysis.

The accuracy of the room-temperature reflectance and high-temperature emittance measurements were verified through a round-robin experiment, and preliminary results are shown. Geometry corrections need to be correlated, the AZT, NREL, SOC, and SNL (when received) data need to be compared, and incident-angle measurements need to be analyzed. The high-temperature measurements need to be compared to the blackbody calculation of the room-temperature measurements. The final results and conclusions of the round-robin testing must be reported.

The durability and thermal stability of commercial (e.g., Solel, Schott) and NREL’s prototype solar-selective coatings will be determined by exposure in the high-temperature inert-gas oven. Results will be examined and used to improve the advanced solar-selective coating. As data become available, development can begin of a criterion for high-temperature selective surfaces applicable for concentrating applications.

ACKNOWLEDGMENTS

The authors wish to acknowledge their colleagues at NREL and Sandia for their contributions. DOE supported this work under Contract No. DE-AC36-99GO10337.

REFERENCES


...


