Solar Absorbing Ceramic/Glass Coatings Increasing the Efficiency of Environmentally Friendly Energy Production

Submitted by Mark O. Naylor
Under Dr. Doreen Edwards

Work performed
June 1 to August 1, 2005

Ceramic/glass coatings for recycled concentrating solar power collector tubes were fabricated to increase chemical and thermal durability to reduce waste of current CSP operations. Thin coatings with 10 volume % solids loading had solar absorption of 0.82 to 0.94 with the goal of 0.95 to 0.98. Low thermal emissivity of 0.1 was not achieved. The best performance was by 1 μm coatings of 5 volume % which absorbed 0.91 to 0.94 at CSP operating temperatures of 400 °C. Efficiency of CSP technologies could increase possibilities of industrial turnover to environmentally cleaner forms of energy production.

Submitted to:

Alfred University
Center for Environmental and Energy Research (CEER)
Alfred, NY 14802
October 5, 2005

Introduction

Concentrating solar power (CSP) trough plants use parabolic trough collectors that concentrate sunlight to create high temperature heat. The inefficiency of modern methods of concentrating solar power trough plants is primarily due to the vapor-phase-deposited molybdenum coating on the SS tubes.

The coating, at operating temperature, requires seclusion from air by maintaining a vacuum between itself and a surrounding borosilicate glass tube. Stresses at a glass-to-metal seal fail due to thermal expansion differences as a consequence of extreme temperature differences during the days and nights in the desert, and the required vacuum is lost leading to oxidation of the molybdenum. The oxide no longer provides thermal efficiency and lacks the required thermal and optical properties of metallic molybdenum. The tube loses efficiency and must be replaced.

These failed tubes can be recycled to reduce waste if new coatings are engineered. The increased efficiency with spectrally selective coatings will decrease costs associated with solar power, and CSP could become a cost effective means of clean energy production.

Ceramic/glass enamels will be developed which tolerate temperatures higher than are reached during CSP operation. The need for a vacuum will diminish if not be eliminated, which will avoid complications of currently used collector tubes. Thickness, pigment loading, firing temperature, optical, and thermal properties will be engineered to create an affordable and reliable coating.

Methods

Square, 18 gauge, stainless steel (SS) samples having 2x2 inch dimensions were obtained. The squares were sandblasted with ≈24 psi with the nozzle 5.75 in from the substrates. Both sides were blasted to produce a flat substrate to facilitate the coating process. A commercial glass/ceramic frit was obtained to begin the baseline coating process. Terpineol Ethyl Cellulose (TEC) was used as a binder for the frit having a low viscosity. Solids loading was varied from 40-20 volume % initially. The paste was mixed on a tri-mill for proper dispersion of the frit in the TEC. The pastes were applied by a screenprinter to the SS substrates immediately after mixing. The printed coatings were flawless and were allowed to air dry for about 24 hours. A fast-firing sequence was mimicked to observe production scale rates. The process proved success. Final temperatures ranged from 600-800 °C to observe correlating effects.

The thermal and optical properties of the samples were analyzed through IR absorbance and diffuse reflectance spectroscopy, respectively. FTIR reflectance was measured from 2,500-15,000 nm wavelengths at RT to 400 °C in 100 °C increments. IR emissivity is typically reported at 400 °C. Diffuse reflectance spectroscopy measurements were performed at 8° normal incidence from 250 to above 2,500 nm wavelengths.

The surface roughness was characterized with an Interferometer. An average value of peak to valley, known as the root mean square value (RMS), quantitatively describes the studied surface.

Variables were minimized. A dental furnace was purchased to precisely produce the fast firing sequence. The frit was sieved to produce coatings of more a uniform particle size of about 53 μm. Pastes were passed through the tri-mill three times before screenprinting. The tri-mill and screen were meticulously cleaned to increase experimental repeatability. Pastes of lower solids loading down to 5 vol % were mixed to obtain near 1 μm coatings. Optical and thermal data was analyzed to observe trends and relations to final holding temperature and solids loading.

The coatings produced, after variable minimization, were cross-sectioned to determine coating thickness with the Environmental Scanning Electron Microscope. Thickness was then related to the optical and thermal trends.

Three clear enamels were mixed with a Ferro pigment attempting to cater the ceramic/glass ratio in the processing variables. After some firings, the Ferro enamel had the best results. Pigment content was varied in the solids loading to relate the optical and thermal properties to pigment loading in constant solids loading conditions. A study of four pigments was performed to find the most optimally performing pigment.

Results

Lower firing temperatures were sought to increase surface texture. A constant solids loading of 30 vol % was fired with hold temperatures of 675 to 800 °C. The surfaces of the coatings were analyzed with the interferometer and the range of root mean square (RMS) values were obtained. A higher RMS value relates to higher surface texture. The 800 °C sample was very smooth compared to the rough surface of the 675 °C sample.

Low solids loading was desired to create thin coatings, which were assumed to perform optimally as specific absorption materials. The low solids content also facilitated high surface texture due to the sandblasted substrates. Thinner coatings more readily mimicked the surface of the blasted steel. Firing temperatures were held constant at 650 °C to prove the 5 vol % coatings had rougher surface textures than the higher solids loadings.

Coating thickness varied due to solids loading content. The 40 vol % coatings produced a thickness of 38 μm, while the 20 and 5 vol % coatings provided a thickness of 15 μm and 1 μm, respectively. The solids loading facilitated screenprinting while allowing coating thickness control.

Coatings from 40 to 20 vol % covered the surface of the substrate completely and had very little variation in thickness. The variance decreases as the solids loading increases, however the trend is deviated at 40 and 5 vol %.

The 5 vol % coating achieved the desired 1 μm thickness. Increased surface texture of the coating disallows observation of a smooth coating when viewed by cross-section. The thin coatings collect in the valleys of the textured steel.

The IR absorption for stainless steel at 400 °C is about 70 to 80 %. Ideal coatings would have mid-IR absorption near 10 % at 400 °C. The ceramic/glass coatings exhibit absorption that ranges from 80 to 99 % at 400 °C. The lower solids loading coatings provide lower emissivity over more of the IR range. The 5 vol % coating shows no higher than 95 % absorption and 90 % absorption at about 6,300 nm wavelengths. Its performance is the most selective of the currently studied coatings and warrants more attention.

The ultra-violet, visible, and near-IR measurements were performed to observe the most crucial properties of the coatings. Ideal performance of coatings would involve maximum absorption of 95-100 % from 250 to 1300 nm with a sharp drop to 10 %

absorption at 1300 nm. The 10 vol % coating, fired to 650 °C, presents the most selective properties which absorb 90-92 % in the UV, and 87-90 % absorption in the visible range. The slope decreases more in the 10 vol % coatings than in any other solids loading. The 20 vol % coating only absorbed 89-91 % in the UV, 86-88 % in the visible, and absorbed more near-IR than the 10 vol % coating. The 30 and 40 vol % coatings absorbed up to 93 % of the visible wavelengths, however the IR absorption was much higher than the 10 and 20 vol % coatings. Lower solids loading produced more optimal performance at 650 °C.

The 10-40 vol % coatings fired to 750 °C all absorbed about 93 % of the UV spectrum into the onset of visible wavelengths. A deviation occurred in the visible spectrum where the 20-40 vol % coatings absorbed 87-94 %, and the 10 vol % coating absorbed 82-93 %. The 20-40 vol % coatings exhibited poor near-IR absorption of 84-91 %, while the 10 vol % coating was more selectively absorbing 77-86 %. Selective absorption trends began with lower solids loading and higher firing temperatures. The 10 vol % coating absorbed similar UV and visible wavelengths as the other coatings, while achieving more selective emissivity in the near-IR range.

Discussion

The selected firing temperatures were well above the requirements of CSP technologies. Lower temperatures offer cost savings, yet robust performance requires relatively durable coatings. A lack of durability is reached as the firing temperature decreases due to reaching the glass transition of the frits. Some of the coatings fired at 650 °C could be rubbed off. The low-fired coatings also produced the high surface texture to provide scattering, but the higher temperatures offered optimal UV-vis absorption. Maximum absorption of visible wavelengths is essential to CSP methods of energy production, so higher firings were becoming the focus near the end of the project. This was contradictory to assumptions early in the process.

The thinner coatings provided better UV and visible absorption as well as more selective absorption of the near-IR range of wavelengths. The 5 ol v% coatings had not been tested for UV absorption, however their performance in the far-IR range was more selective than the 10 vol % coatings. The thinner coatings are nearing the goal of selective absorption materials. The goal of UV-vis absorption is 0.95 to 0.98, and the materials absorbed well reaching values of 0.82 to 0.94 with the thinner coatings. The absorption in the far-IR presented a large problem compared to the UV-vis. The goal of 0.1 is far from accomplished. The 5 vol % coatings fired at 650 °C reached 0.91 at the lowest peak, and averaged over the 2,500-15,000 nm range at about 0.94. Unfortunately the coatings exhibit IR absorptions that are opposite the desired behavior. The IR behavior must be tailored.

A study was performed using a single enamel with different pigments, but a complete study of their properties was not completed during the summer investigation. Thin coatings of four different pigments were made with low solids loading and were fired; the results will be published in a future CEER report. Higher UV-vis absorption was the overall goal. The IR absorption properties were most likely similar to the results in this study.

Conclusions

Recycling of the parabolic collector CSP tubes has been deemed possible through this process. Thinner coatings provide better performance in CSP conditions requiring less material to be purchased. The behavior of the ceramic/glass frits has been tailored through firing temperatures and thickness control of the coatings. Solids loading successfully controlled the thickness of the coatings down to 1μm. The absorption in the UV and visible portion of the spectrum was about 0.82 to 0.94 for the thin coatings; their performance is near the goal of 0.95 to 0.98. The IR absorption of the ceramic/glass frits is undesirable. The absorption is about 0.91 at best, which is poor compared to the goal of 0.1.

The IR absorption properties need to be controlled in further studies. Secondary coatings are thought to provoke lower absorption in the near and mid-IR. Several coatings should be investigated for selective absorption. The composition of the enamel could be tailored to meet the necessary IR absorption. Enamel composition in the frits could be changed to shift the near IR edge to higher wavelengths resulting in less IR absorption.

A process must be created to coat the reusable stainless steel cylinders. The temperatures for the recycling process will be higher than desired, yet the materials analyzed in this study are as cheap and selective as possible. The recycled tubes with these thin coatings will perform without a vacuum-sealed atmosphere even at 500°C. The coatings will be durable and replacement of the collector tubes should not be necessary. The environmentally friendly process of CSP can gain acceptance as reliable and efficient means of energy production.

Works Cited

1) Kennedy, “Review of Mid- to High-Temperature Solar Selective Absorber Materials”, *National Renewable Energy Laboratory* (July 2002)
2) Messele, Carl. "Screen Printing Primer - Part 3." Hybrid Circuit Technology (1985): 11-13.
3) Missele, Carl. "Screen Printing Primer - Part 1." Hybrid Circuit Technology (1985): 11-13.
4) Missele, Carl. "Screen Printing Primer - Part 2." Hybrid Circuit Technology (1985): 11-13.
5) 25 Sept. 2005 <http://http://rredc.nrel.gov/solar/spectra/am1.5/ASTMG173/ASTMG173.xls>.