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Copper-oxide spinel absorber coatings for high-temperature concentrated solar power systems

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ABSTRACT

Concentrated Solar Power (CSP), a promising renewable energy technology, involves methods to concentrate the sun's energy onto receiver systems that generate steam, activate turbines, and consequently generate electrical power. To ensure CSP technologies remain cost-competitive, absorber coatings on CSP receiver systems require performance enhancements for increasing solar-thermal energy conversion efficiency. In this work, black metal-oxide nanoparticles comprising copper-cobalt oxides ($Cu_xCo_{3-x}O_4$) and copper-manganese oxides ($Cu_xMn_{3-x}O_4$) are synthesized for solar absorptive potential by hydrothermal syntheses – selected for low-cost, energy-efficient fabrication capable for bulk manufacturability. The material is deposited onto high-temperature, durable Inconel substrates by a flexible spray-coating method, and characterization is performed by Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS), and X-Ray Powder Diffraction (XRD) analyses, as well as measurements to gauge thermal performance. High temperature stability of a model solar receiver surface using these synthesized materials are assessed by comparing spectral reflectance and a figure-of-merit efficiency metric before and after high temperature exposure beyond 1000 h. To extend spectrally-selective absorbance capability, the coating surfaces are geometrically-textured using sacrificial polymer beads that are jointly implemented in the spray-coating process. This study ultimately showcases materials produced with high figure-of-merit conversion efficiency, demonstrating solar absorber coatings capable of interfacing with next-generation CSP receiver systems.

1. Introduction

Concentrated Solar Power (CSP), a solar-thermal type of power generation, contrasts with standard photovoltaic arrays in that it drives turbines and generates electricity from stored heat [1,2] rather than converting photons to electrons directly via the photoelectric effect [3]. For large-scale power installations, despite the requirement of larger geographic area, CSP is favored due to its much lower construction and operating costs [4]. Electrical power generation by such solar-thermal methods are attractive contenders for solar-favorable geographic areas, as they provide a competitive avenue in the market for renewable energy production [5,6]. Compared to photovoltaic arrays, CSP features storable energy at times of limited or null solar insolation, higher energy conversion potential, and the ability to retrofit older power plant installations for a reduced environmental footprint [7,8]. Ensuring the cost-effectiveness of CSP platforms require meeting an operating cost target of 5.5¢/kWh, which are enabled through maintaining elevated thermal and exergic efficiencies at higher system temperatures ($T \geq 700$ °C), maximizing electric power output from solar-thermal energy conversion [9]. Therefore, the ability to minimize energy loss from waste heat, or to streamline material manufacturability and operating conditions [10], is vital for reducing the levelized cost of energy (LCOE), a metric that accounts for associated system-level expenses for maintaining CSP power generation longevity [11].

Optimizing reliable operating conditions in such capacities, especially with regard to temporal material efficiencies used in the CSP system, helps to meet the United States Department of Energy (DoE) and International Energy Agency (IEA) benchmarks for significantly improving LCOE [12]. According to budgeting considerations in the U.S. DoE SunShot Initiative [13], energy-efficient technologies are predicted to be best suited to the 'power tower' CSP design (one of many overall CSP plant configurations) as this correlates to the design intent of next-generation utility-scale plants that minimize LCOEbased on higher achievable solar concentration compared to parabolic trough CSP systems [14]. Such a setup includes reflector arrays, mounted heliostats, or Fresnel-lens let concentrators to subsequently combine with a thermal storage receiver, using coating materials to absorb the sun's energy onto a receiver platform containing a high-temperature working

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fluid [15,16]. The selection of specialized coating materials on both highly reflective heliostats that concentrate the sun's energy, as well as absorptive receiver systems, have a large influence on the thermodynamic efficiency of the CSP energy conversion process [17–19]. While absorber coating materials are generally optimized to ensure high absorptivity in the dominant ultraviolet and visible regions of the solar energy spectral range, increasing the system operating temperature reduces the CSP collector efficiency despite overall boosts in overall heat engine efficiency [20]. Emphasis is given on solar absorber materials for CSP receiver systems, ensuring greater energy conversion with coatings that are efficient at high temperatures [21].

Various configurations concerning the preparation of solar absorbers range from intrinsic coatings, to the more complex semiconductor arrays [22], ceramic-metal composites (cermets) [23], and the possibility of porting any of the aforementioned to multilayer coatings [24]. While a review by Atkinson et. al. [25] suggests that intrinsic absorber coatings are not suitable for extremely high temperatures compared to reinforced multilayer coating designs, intrinsic absorbers are the easiest to manufacture, and structural treatment and modifications to some classes of materials, such as hafnium carbide (HfC) or silicon carbide (SiC) demonstrate promise for intrinsic absorber coating types due to the materials' high melting points [26]. As most cermet coatings are sensitive to oxidation and performance degradation above $T = 500$ °C, viable CSP absorber coating candidates, as featured in Kennedy et. al. [27], rank the suggested effectiveness of inorganic oxide materials. While such recommended materials survive at high temperatures, many intrinsic coating types are not projected to inherently feature spectrally-selective behavior – coatings that absorb most solar irradiance while rejecting higher wavelengths that re-emit thermal energy, equating to energy loss characteristics through waste heat. However, intrinsic coating types may inherently feature greater cost-effectiveness and long-term reliable operation [28], based on material availability, ease of synthesis, and maintainability [29]. It is noted, while spectrally-selective behavior is a performance enhancement at higher operating temperatures, if a CSP system also maintains high concentration factors, the favor of spectral-selectivity is effectively nullified since increasing solar concentrations minimizes contributions of thermal energy loss.

To summarize, for next-generation CSP material coatings, research milestones for energy-efficient solar absorbers include:

1. Higher-temperature operation ($T \geq 750$ °C) to increase the extent of allowable absorbed energy (an optimal CSP operating temperature is predicted by the Stefan-Boltzmann Law).
2. Streamlined manufacturability and coating deposition of absorber material onto CSP receivers, reducing operating costs.
3. Spectrally-selective absorptive response, improving upon industry-standard paints, to limit waste heat at higher wavelengths (thermal losses through spectrally-dependent re-radiation predicted by the Planck Radiation Law), especially when operating at higher temperatures and low concentration factors.
4. Reliable performance at a selected CSP operating temperature survivable by absorber materials and other system components, where the optimal selection of solar concentration allows for the best overall solar-thermal conversion efficiency by high UV–Vis absorptance and low IR emittance.

A variety of candidate materials consisting of inorganic oxides were surveyed for their operational reliability and manufacturability, given their air-stable behavior and high-temperature stability. A review by Suman et. al. [30] reports on the economic need for the manufacturability of coatings compatible with absorber surfaces, rather than the CSP configuration type used. Kumar et. al. [31] prepared CuO nanostructures on Cu substrate via an oxidation synthesis that averaged 84–90% absorptance and 6–7% emittance. However, such spectrally-selective behavior may come at the cost of lower material lifetime, where diffusion into the absorber layer does not support phase stability [32]. A poly-metallic coating containing Cu, Mn, and Co, was synthesized by Tulchinsky et. al. [33] resulting in a high-absorptance coating that did not exhibit notable spectrally-selective behavior, though comparable copper-containing candidates were shown to have promising optical performance and high-temperature absorptance response in the UV–Vis spectral range. Pyromark® 2500 paint (an industry standard and reference material) is shown to contain a major Cu-Fe-Mn constituency [34], and it generally survives a maximum working temperature of $T = 500$ °C $-$ 550 °C, with paint coating re-application required semi-annually. However, Pyromark® classes of paints experience low emissivity at higher IR wavelengths and degradation at too high of operating temperatures. Possible improvements to this material include a patented method reported by Bayón et. al. [35] that demonstrates the synthesis of copper-manganese spinels by a dip-coating method, resulting in a spectrally-selective absorber material that averaged 94% absorptance and 6% emittance. Notably, relative stoichiometric detail of mixed copper-oxides (including cobalt and/or manganese) [36-42] concluded that spinel phases of $Cu_{1.5}Mn_{1.5}O_4$ or $CuMn_2O_4$ were synthesized to achieve low thermal emissivity, absorptance improvements in the ultraviolet and visible region, as well as reliability at higher operating temperatures above $T = 500$ °C motivate further study.

Our previous work demonstrated cobalt oxide nanoparticles that were reported to have desirable solar absorbing properties at high-temperature operation of $T = 750$ °C [43]. This study specifically investigated nanoparticle syntheses of copper bi-metallic oxides, (copper-cobalt oxide spinels of types $Cu_xCo_{3-x}O_4$ and copper-manganese oxide spinels of type $Cu_xMn_{3-x}O_4$), with a synthesis adapted and modified from previous studies [44], implementing facile spray-coating deposition onto Inconel-625 coupons. Hydrothermal methods were used to create cuprous bi-metallic inorganic oxide nanoparticles – these syntheses allowed for greater control of material crystal properties to derive pure mixed materials. Specifically, inorganic chlorohydrate precursors were reacted and treated via hydrothermal and co-precipitation syntheses, as they resulted in metal-oxide nanoparticles that were later annealed and ball-milled under specific conditions to adjust nanoparticle sizing.

This study demonstrates the utility of intrinsic absorber coatings based on surface-textured performance enhancements – improved spectral absorptive response from light-trapping structures that are capable of surviving higher CSP operating temperatures. Fabricated cuprous oxide-based nanoparticles, when ported to a viscous slurry via a silicon dioxide (SiO_2) binder, were optionally treated with sacrificial polymer beads (SPB) made of poly(methyl-methacrylate) of diameter $D_{SPB} = 1 - 5$ µm to explore possibilities for effectively surface-texturing different light-trapping geometries. In contrast to sol-gel/dip-coating methods for sample preparation, a facile spray-coating method was employed in our synthesis to optimize for low-cost, energy-efficient processing capable of bulk-scale manufacturability. While the proof-of-concept for qualifying materials as feasible for high-temperature system operation or spectrally-selective response are generally produced by sputter-coating or electroplating methods, this work demonstrates spray-coated samples with improved durability, measurement repeatability, and reliability – by the proposed synthesis methods, this cost-effective avenue is tenable for CSP system longevity. In upscaling, we implemented process optimizations for the reduction of waste by-products, low-cost of process reactants, and ease of synthesis while producing high-purity materialswith high UV–Vis solar absorptance and minimal IR thermal emittance achievable with high CSP operating temperatures and solar concentration factors.

2. Theory and calculation summary

For maximizing energy conversion efficiency, the material absorber efficiency η_{abs}, defined as a ratio of absorbed solar irradiation to total available incident solar energy, can be expressed analytically as follows, representing time-averaged spectral reflectance of the figure-of-