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Fabrication and characterization of multiscale, fractal textured solar selective coatings

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ABSTRACT

Photothermal conversion efficiency depends significantly on the selectivity of the thermal receiver surface through which a heat transfer fluid flows in a concentrated solar power system. This paper presents studies on novel multiscale, fractal textured solar selective coatings for solar thermal applications. The fractal surfaces are fabricated integrally on the substrate material using electrodeposition. The coatings are described in terms of fractal parameters that are uniquely determined from surface measurements, and the optical properties of the coatings are experimentally characterized in detail in terms of the fractal parameters. The effects of heat treatment on the optical properties of coatings over a range of fractal parameters are also described. The study is presented considering coatings on copper to demonstrate that fractal texturing of the surface provides a nearly three-fold performance improvement compared to coatings with no texturing or heat treatment. The findings equally apply to other materials used in higher temperature solar thermal applications.

1. Introduction

The recent years have witnessed a sharp increase in efforts towards efficient energy generation using renewable resources such as solar, wind etc. Concentrating solar power (CSP) generation is of significant interest amongst the various approaches used to harness solar energy [1]. One of the major advantages of CSP is the ability to incorporate inexpensive and highly efficient energy storage in thermal form, which can provide electricity generation in periods with no sunlight as well [1,2]. Power generation with CSP involves five major steps: (i) concentration: tracking and concentrating sunlight onto a solar receiver, (ii) absorption: incident solar energy on the receiver is converted to heat by an absorber, (iii) transfer: heat carried away from the absorber by a heat transfer fluid (HTF), (iv) generation: utilization of thermal energy for power generation in a heat engine, and (v) storage: excess heat stored in an efficient and cost-effective thermal energy storage.

The goal of a thermal receiver in a CSP plant is to effectively absorb sunlight with minimal thermal loss. Therefore, improving the photothermal conversion efficiency of CSP systems is of considerable interest [3–8]. Photothermal conversion efficiency depends primarily on the selectivity of the surface carrying the HTF. An ideal absorber must exhibit high spectral absorptance (> 0.95) in the visible and near-infrared (IR) wavelengths (0.28–2.5 μm), where the bulk of the energy from the solar spectrum is concentrated, and low emittance (< 0.1) in the IR wavelengths ($\sim$ 2–20 μm), where the black body emission peaks. To achieve the desired optical properties, solar selective coatings are applied on the base metal substrates. To this end, several solar selective coatings with different properties, materials and deposition techniques are reported in the literature [3–8]. The coating material and its microstructure are the primary parameters defining the optical properties, and coating microstructures are largely dependent upon the deposition process and parameters [9].

In general, coatings fabricated through industrially scalable techniques such as electrodeposition, spray coating, dip coating etc., exhibit multiscale, randomly rough morphological characteristics [9–11]. Several researchers have characterized the optical properties of such coatings based on their roughness [10–13]. Through experimental studies, it is shown that the roughness of coatings is positively correlated with their effective solar absorptance and thermal emittance [10–13]. Additionally, coating surface roughness has also been modeled using Gaussian disorder by Kowalczewski et al. [14] who estimated the optimum roughness parameters yielding the highest absorption enhancement. However, as presented by Majumdar and Bhushan [15–17], conventional roughness parameters, such as root-mean-squared (RMS) height, slope and standard deviation, are not unique to a surface and depend on the scan length and resolution of the measuring instrument. In addition, Kang et al. [18] also concluded based on analysis of machined surfaces that the standard surface parameters such as roughness and slope are not sufficient descriptors of surface characteristics, as the surface topography is non-stationary and multiscale in

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nature. The studies suggest that fractal parameters, owing to their invariance with length scale [18], are better suited for description of surface topography.

Characterization of coatings based on fractal theories has been used in the description of elastic-plastic contact [15–17], tribology [17] and tool wear [18]. However, application of scale-independent fractal description to understanding the optical properties of solar selective coatings remains rather limited in literature. Recently, Barrera et al. [9] applied detrended fluctuation analysis (DFA) to scanning electron micrographs (SEM) of black Mo coatings on copper substrate to study their fractal properties. Furthermore, correlation of fractal parameters with the optical properties demonstrated an increase in absorptance and emittance of coatings with growth of fractal nature of surface [9]. However, an energy dispersive spectroscopic (EDS) analysis revealed the presence of multiple elements such as Mo, Cu, O, on the coating surface, and a variation in coating material composition is expected for coatings generated at different processing conditions. Due to this variation in material composition between coatings, the results do not provide a clear effect of fractal parameters alone on the optical properties of coatings. In addition, the dip coating process considered to fabricate the black Mo coatings leads to fractal dimensions only in a small range of 1.02–1.2. It is evident from the foregoing discussion that the studies so far primarily use scale-dependent roughness parameters, which are not the best descriptors for multiscale coatings, or have explored coatings with surface textures over a small range of fractal dimensions.

It may be conceptually argued that surfaces with highly multiscale asperity features that have high fractal dimensions will have enhanced photothermal conversion, and the present work seeks to explore this hypothesis. To systematically elucidate the effects of surface texture on the optical properties of coatings, the goals of the present work are: (1) fabrication of multiscale, fractal solar selective coatings integral to the base metal through electrodeposition, where the fractal dimensions can be tailored by adjusting the process parameters, (2) description of the fabricated solar selective coating topographies using scale-independent fractal parameters and (3) systematic analysis of the optical properties of the coatings in terms of the fractal parameters. A two-step electrodeposition technique developed by Haghdoost and Pitchumani [19] was considered in this study to fabricate stable multiscale coatings. The fabricated coatings are mathematically characterized based on the Weierstrass-Mandelbrot (W-M) function [16,17], and the fractal parameters of coating surface are uniquely determined through the power spectrum of surface based on noncontact profile scans. The effects of applied deposition potential and heat treatment on the coating morphology, fractal parameters, and optical properties are studied and described in detail. The study is presented considering coatings on copper to systematically elucidate the effect of multiscale fractal texturing of the coatings on the optical properties. However, the results of the study apply to other materials as well for higher temperature CSP applications.

The article is organized as follows: the experimental methods and fabrication techniques are discussed in the next section, which is followed by a fractal description of surfaces and estimation of their fractal parameters. The results on SEM morphologies of the coatings, and their fractal and optical characterizations, as well as the effects of heat treatment are presented and discussed.

2. Experimental methods

2.1. Materials

Analytical grade Copper sulfate ($CuSO_4$, 99 + %), Sulfuric acid (H_2SO_4), Acetone (99.5 + %), and Methanol (99.5 + %) were purchased from Fisher Scientific, USA and used as-received without any further modification. Copper sheets (99.9%) used in the studies were purchased from McMaster Carr, USA. All the electrolyte solutions were prepared using deionized water with a resistivity of 18 MΩ cm.

2.2. Fabrication of copper-based selective coatings

Solar selective coatings on copper substrates were fabricated using the two-step electrodeposition process, as described by Haghdoost and Pitchumani [19], to generate robust and durable electrodeposited coatings. An AUTOLAB PGSTAT128N potentiostat supplied by ECO chemie, Utrecht, The Netherlands, was used to perform the electrodeposition experiments. The fabrication process used the traditional three electrode system, with platinum mesh as anode, copper sheet as reference electrode and copper sheet with an exposed area of 1 cm^2 as working electrode. All the electrodes were rigorously cleaned with acetone, methanol and deionized water to remove any dirt and grease from their surfaces, and dried in air. The electrolyte was an aqueous solution containing $CuSO_4$ (1 M) and H_2SO_4 (0.5 M). The solution was deaerated by bubbling it with nitrogen for 15 min prior to the fabrication of each sample. Since the reference electrode and the working electrodes were made of the same copper sheet, the electrode overpotential is used to indicate the applied potential. Furthermore, electrodeposition was performed at various overpotentials ranging from 0.5V to 1.1 V, to study the effects of applied overpotential on the fractal properties and optical properties such as solar absorptance and emittance of the coatings. Deposition times were optimized to obtain the same deposit thickness of about 30 μm for all the samples fabricated at the various deposition overpotentials. It was identified by Haghdoost and Pitchumani [19] that application of a low overpotential for a short duration after deposition at a high overpotential leads to a stable coating with multiscale morphology. Accordingly, in the present study, electrodeposition at overpotentials above 0.9 V was followed by deposition at 0.15 V for a duration of 10 s. After electrodeposition, the surfaces were rinsed with acetone and deionized water and dried with nitrogen gas.

2.3. Characterization

The surface morphologies of the deposited coatings were examined using the FEI Quanta 600 scanning electron microscope (SEM), which was operated at 10 KeV for electron imaging. EDS measurements were also performed using the same instrument.

A Zygo NewView 8000 series 3D optical surface profiler was used to perform profilometric measurements on the prepared copper based solar selective samples. The instrument uses coherence scanning interferometry to measure the surface profile and provide non-contact, highly accurate and quick measurements of the prepared surfaces. Fig. 1(a) shows an example measured profile on one of the fabricated samples. The measured profile scan data was processed through the image and surface analysis software Gwyddion [20] for profile visualization and analysis. Surface profile scans were performed at three different locations for each sample. For each sample corresponding to a specific combination of material and processing condition, profilometric scans were performed on three replicates and the fractal parameters are presented as average and standard deviation of the obtained data. Surface profile data obtained through the above procedure was analyzed using the software Gwyddion and MATLAB to obtain its averaged Fourier transform based power spectrum. In the present analysis, a radially averaged power spectrum was used to consider the effect of asperities throughout the surface. Using the obtained power spectra for the individual surfaces, their corresponding fractal parameters were obtained as described in the next section on the mathematical description of the multiscale random surfaces.

Furthermore, a figure of merit (FOM) of the prepared coatings was evaluated based on their solar absorptance (α_s), emittance at 2500 nm ($\varepsilon_{2500\ nm}$), and thermal emittance at 80 °C ($\varepsilon_{80\ ^\circ C}$) as described by Ambrosini et al. [21] Diffuse reflectance for the fabricated samples was measured in the range of 0.28–2.5 μm using a Cary 5000 UV–vis–NIR