ENERGY-EFFICIENT SOL-GEL PROCESS FOR PRODUCTION OF NOVEL NANOCOMPOSITE ABSORBER COATINGS FOR TUBULAR SOLAR THERMAL COLLECTORS

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ABSTRACT

The energy efficiency of production processes for components of solar energy systems is an important issue. Other factors which are important for the production of products such as black selective solar coatings include production speed, cycle time and homogeneity of the coating, as well as the minimization of the quantity of the needed chemical precursors. In this paper a new energy efficient production process is presented for production of optically selective coatings for solar thermal absorbers. The latter should ideally behave as a black body, absorbing a maximum of the incoming solar radiation, while minimizing energy losses by infrared radiation, acting as an infrared mirror. The used method to produce such coatings is sol-gel dip-coating

The optical and morphological properties of the Cu-Co-Mn-Si-O based triple layer have been characterized by spectrophotometry, electron microscopy and time of flight secondary electron microscopy. After optimization of the multilayer design, a solar absorptance of 0.95 and a thermal emissivity of 0.12 at 100°C have been achieved. The intermediate Cu-Co-Mn-Si-O layer was analyzed by high resolution transmission electron microscopy. The likewise obtained images show an agglomeration of crystalline grains with 10-20nm in diameter. Therefore, we can consider that the Cu-Co-Mn-Si-O phase is nanocrystalline. In order to roughly estimate the corrosion resistance of the coating in an acidic environment, a simple corrosion test in harsh conditions was designed. With respect to a commercially available durable black chrome coating, this test of corrosion resistance confirmed the durability of the novel sol-gel coating in an acidic environment.

Moreover, the excellent stability at elevated temperatures in ambient air makes the coating an interesting candidate for solar applications involving concentrated solar radiation, such as the generation of solar electricity (concentrated solar power), industrial process heating and solar cooling. For that reason, prototype coatings consisting of stacks of three individual layers were deposited on 2 meter long stainless steel tubes.

Keywords: selective solar absorber coatings; nanocrystalline spinel; induction heating; receiver tubes for concentrated solar power (CSP)

INTRODUCTION

The energy efficiency of production processes for components of solar energy systems is an important issue. One key element of solar thermal collector is the optically selective coating on the solar absorber, which should ideally behave as a black body, absorbing a maximum of the incoming solar radiation, while minimizing energy losses by infrared radiation, acting as an infrared mirror.

Different types of selective absorbing surfaces exist which are described in detail by Agnihotri et al. [1]. Selective coatings for solar thermal collectors are either produced by traditional electrodeposition of black chrome [2], as selective paint [3], or by vacuum deposition processes such as reactive evaporation or magnetron sputtering [4-5]. In the electroplating process, toxic Cr(VI) ions are used and care has to be taken to avoid environmental pollution. On the other hand, vacuum deposition leads to large front costs because of the expensive equipment required and can be out of reach for potential producers in certain situations.

This explains the interest in developing a sol-gel process for the production of nanocomposite selective solar absorber coatings. Indeed, sol-gel processing does not require expensive vacuum equipment and allows to completely avoid the use of toxic chrome. Kaluza et al. [6] demonstrated that it is possible to reach a solar absorptance of 0.86 and a thermal emissivity of 0.11 by sol-gel method with a single layer of CuCoMnOx. Using sol-gel spin-coating, Boström et al. [7] obtained competitive properties for multilayered coatings with nitrogen annealing: Al2O3:Ni multilayered coating absorbs 97% of the incoming solar energy for a thermal emittance lower than 0.05. Recently, Bayón et al. [8] obtained highly selective coatings based on Cu-Mn-Si-O oxides that show excellent optical performance. A solar absorptance of 0.95 combined with a thermal emittance of 0.035 was achieved for coatings on aluminium substrates.

Because of its mechanical stability and the possibility of welding, stainless steel is an interesting substrate material. It can be used for cushion absorbers for domestic hot water generation, and also for receiver tubes for applications working with concentrated solar power (CSP) such as power plants for solar thermal electricity generation, co- and tri-generation. Targeting stainless steel substrates, we focus in this work on the development of multilayered sol-gel coatings for solar absorbers consisting of mixed copper, cobalt, manganese and silicon oxides (Cu-Co-Mn-Si-O). Using suitable multilayer designs, we are aiming for a solar absorptance above 0.94 and a thermal emissivity below 0.16. The coatings shall be deposited with satisfactory homogeneity on stainless steel sheets as well as on collector-sized tubes.

METHOD

The used method to produce such coatings is sol-gel dip-coating for which all the solutions have been synthetized at the Solar Energy and Building Physics Laboratory of EPFL. Solutions were obtained by dissolving the precursors in a solution based on a mixture of absolute ethanol and demineralized water. Nitric acid is added as catalyst to influence both the hydrolysis and condensation rates as well as the structure of the condensed polymer.

The solutions described above were deposited on a stainless steel (austenitic 1.4301) substrate using a dip-coating process. This technique allows to produce coatings even in ambient air at a standard room temperature. The dip-coating process comprises three main steps: dipping of the substrate in the solution, withdrawal at constant speed with formation of a liquid film at the surface, evaporation of the solvent and formation of a xerogel [9]. By thermal annealing between 400°C and 500°C in ambient air, the films are hardened and oxidized.

While the sheetlike substrates were annealed in a Vulcan® benchtop furnace during 90 minutes, a novel, fast and energy-efficient process based on induction heating was developed for the thermal annealing of the 2 meter long austenitic stainless steel tubes [10]. The coated tube was passed through a water-cooled induction coil as described in Figure 1a. An alternative (AC) current oscillating in the induction coil at frequencies between 20 kHz and 200 kHz induces a strong AC current in the steel tube, the latter heating up resistively the tubular substrate as well as the film deposited on it. Using this process, the tube and coating reach approximately 400°C within a few seconds. After a single passage of the induction coil, the radial and longitudinal distribution of the substrate's temperature is sufficiently homogenous as shown by infrared imaging (Figure 1b).

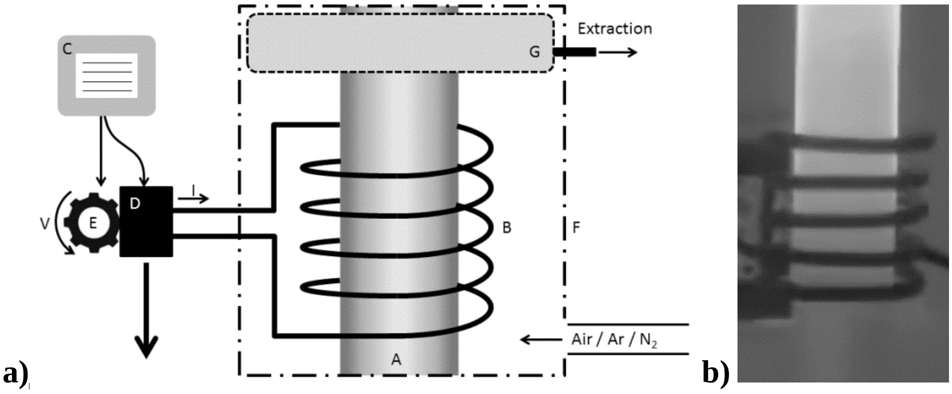

Figure 1a: Schematic representation of the device used for thermal annealing of the coating by induction heating. Austenitic stainless steel tube (A); induction coil (B); control unit (C); AC generator (D); motor (E) rotating at speed V; coil and tube are surrounded by a chamber (F); gasses emitted during thermal annealing are extracted through an exhaust pipe (G). Figure 1b: Infrared imaging of the tube during thermal annealing.

Near-normal spectrophotometric reflectance measurements (380nm – 2500nm) were performed on the produced samples. Using an Oriel MultiSpec 125TM 1/8m spectrograph with Instaspec IITM Photodiode Array Detector and an Optronic Laboratories Monochromator OL 750-M-S coupled to a NIR-sensitive PbS detector (OL 730), the solar absorptance of the coatings can be determined. Additionally, their thermal emittance at 100°C can be measured with an Inglas TIR100 emissiometer.

Structural analysis of different coatings has been performed by high resolution transmission electron microscopy (HRTEM Philips CM300). Bright field images were obtained from cleaved edge single layers deposited on silicon. These images made it possible to obtain morphological information from the deposited films.

In order to know the elemental composition of a multilayered coating on a stainless steel substrate, time of flight secondary ion mass spectroscopy (ToF-SIMS) was performed by means of an IONTOF setup, by reconstructing successive two dimensional (2D) XY measurements from the top-layer down to the substrate. The multilayered coating is composed of three layers of Cu-Co-Mn-Si oxides: Substrate // Cu-Co-Mn-O // Cu-Co-Mn-Si-O // Si-O // air. The layers were deposited successively by sol-gel dip-coating.

In order to roughly estimate the corrosion resistance of the coating in an acidic environment, a simple corrosion test in harsh conditions was designed: a drop of hydrochloric acid 25wt% is deposited on the sample and the degradation time is monitored.

RESULTS

Single layers of Cu-Co-Mn-O on stainless steel were first considered. The solar absorptance of the sample was optimized by varying the withdrawal speed. A solar absorptance of 0.86 ± 0.01 was reached for a thermal emissivity of 0.11 ± 0.01, which is fully appropriate for a single layer coating. The next step consisted in optimizing the solar absorptance of the coating by adding an anti-reflection layer on top of it. The anti-reflection layer used is made of silicon oxide (SiOx). For this double layer configuration, the thickness optimization for individual layers leads to a solar absorptance of 0.94 ± 0.01 for a thermal emissivity of 0.11 ± 0.01.

Optical characterization of the coated samples is shown in Figure 2. The spectral reflectivity is represented as a function of wavelength for a single layer coating (dotted line I) and a double layer coating (dotted line II) on a stainless steel substrate. The same graph also shows the spectral distribution of solar radiation for comparison purposes.

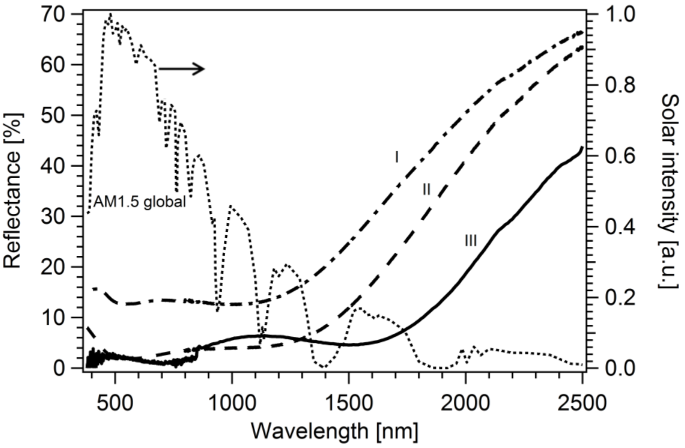

Figure 2: Spectral reflectivity of black selective samples. The dotted line I represents the reflectivity of a single layer coating (substrate / Cu-Co-Mn-O) the dotted line II represents the reflectivity of a double layer coating, (substrate / Cu-Co-Mn-O / Si-O) and the solid line III represents the reflectivity of a triple layer coating on stainless steel (substrate / Cu-Co-Mn-O /Cu-Co-Mn-Si-O / Si-O). The respective solar absorptions are α_{sol}*=0.86 for I,* α_{sol}*=0.94 for II and* α_{sol} *=0.96 for III.*

A graded index coating composed of three distinct layers was then designed. The intermediate layer is a mixture of the bottom (Cu-Co-Mn-O) and the top layer (SiOx). As an intermediate layer favors the light penetration and absorption, it increases the solar absorption of the coating up to 0.96 ± 0.01 with an emissivity of 0.12 ± 0.01.The monitored spectral reflectivity of this sample is also presented in Figure 2 (solid line III). The intermediate Cu-Co-Mn-Si-O layer was analyzed by HRTEM. The figure 3a shows an agglomeration of crystalline grains, 5-20nm in diameter. Therefore, we can consider that the Cu-Co-Mn-Si-O film is nanocrystalline.

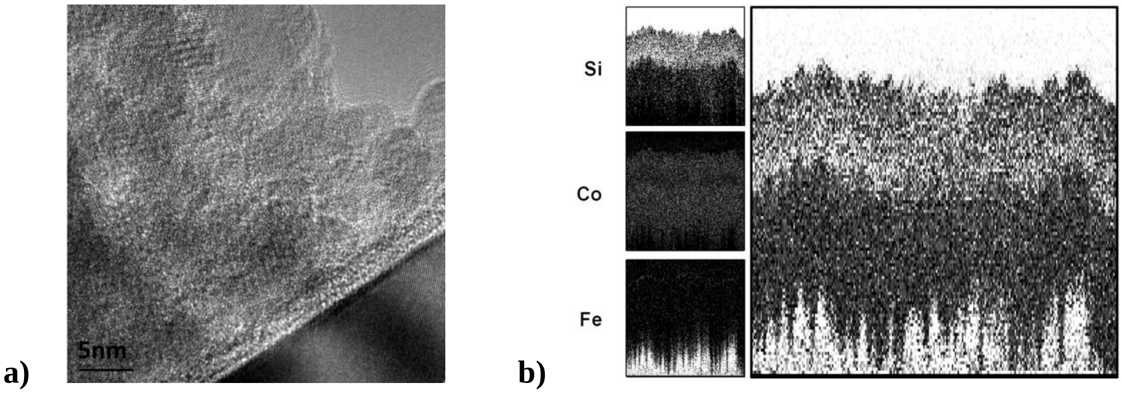

Figure 3a: Nanocrystalline structure of Cu-Co-Mn-Si-O layer by HRTEM. Figure 3b: Analysis of a graded triple layer coating by Tof-SIMS.

Two dimensional (2D) depth profile was performed by ToF-SIMS and element cross section profile is shown in figure 3b. The element specific detection of silicon (Si), cobalt (Co) and iron (Fe) allows the visualization of a stratified coating on stainless steel which confirms the presence of three distinct and superposed layers.

A simple corrosion resistance test confirmed the durability of the novel sol-gel coating in an acidic environment. For the reference black chrome coating, after less than 40 seconds in contact with HCl, a marked variation of colour is observed, reflecting a sharp deterioration of the coating. The sample produced in the laboratory with the sol-gel triple layer coating shows a complete degradation after three minutes instead of less than 40 seconds. These results suggest that the novel coating might be more durable in acidic environments than the conventional black chrome coating for unglazed flat plate collectors.

The excellent stability at elevated temperatures in ambient air [11] makes the coating an interesting candidate for solar applications involving concentrated solar radiation [12], such as the generation of solar electricity (concentrated solar power), industrial process heating and solar cooling. For that reason, prototype coatings consisting of stacks of three individual layers were deposited on 2 meter long stainless steel tubes. Because identical solutions are used for coatings of sheets and the tubes, their chemical compositions remain similar. However, the new production process which is adapted to the cylindrical geometry of the metallic tubes might result in a slightly different phase composition.

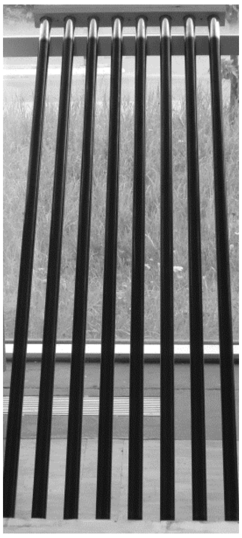

Figure 4: Two meter long black selective tubes produced in our lab using the novel selective coatings applied using the novel deposition-induction process.

For the multilayers obtained by this process, no visible cracks are observed. In addition to that, debonding or peeling effects do not occur, indicating that good adhesion of the individual layers to the substrate and to each other is achieved. The highly reproducible homogeneity of the multilayered coatings on 2 meter long stainless steel tubes is illustrated in Figure 4. The promising results obtained by the novel processing technique demonstrate the commercial potential for sol-gel stacks in concentrated solar power applications.

DISCUSSION - CONCLUSION

Multilayered thin films were designed with the aid of computer simulations based on the method of characteristic matrices. The top-layer used as a corrosion barrier is made of quartz. The challenge was to make this layer very homogeneous with as little porosity as possible. Moreover, controlling the roughness of layers deposited by a wet chemical process was crucial. All these parameters have been mastered to finally produce a coating resistant to hydrochloric acid.

The thermal emissivity of the stainless steel substrate is roughly equal to 0.10 at 100°C. While this value is acceptable for unglazed flat plate collectors, for glazed collectors, a thermal emissivity below 0.05 is preferable. In order to achieve such values, an infrared-reflecting interlayer would have to be added.

In conclusion, this study describes the development of a black selective coating made by sol-gel dip-coating. The optimization of the optical properties led to a solar absorption larger than 0.95 with a thermal emittance close to 0.12. Corrosion and thermal resistance tests demonstrated that the coating is highly durable and may compete with existing commercial options. Finally, a graded coating consisting of a triple layer was successfully deposited on 2 meter long stainless steel tubes which can be used for concentrated solar power plants.

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