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Optical parameters of a novel competitive selective absorber for low temperature solar thermal applications

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ABSTRACT

Up to now many efforts have been put into environmentally friendly techniques for designing high quality selective absorbers to take advantage of the abundant and clean solar energy sources. In this paper a new selective absorber for low temperature thermal applications is presented. It is a multilayered absorber, specifically a three layer configuration, with only one layer of absorber material. It is composed of $CuMnO_x$ thin film and two consecutive antireflective coatings: $FeMnCuO_x$ and SiO_2. The $CuMnO_x$ film and the $FeMnCuO_x$ antireflective layer were prepared from alcoholic solutions containing metal nitrates while the solution used to prepare the SiO_2 coating was prepared from silicon alkoxides. The deposition of the three layers onto the aluminum substrate achieves solar absorptance values of 0.957 and thermal emittance values of 0.038 at 100 °C. In this way, it is obtained a very good selective absorber with three layers configuration by using a simple, reproducible and cost-effective method such as dip coating.

1. Introduction

The generation of heat using the environmentally friendly and free sun energy is the basis of solar thermal collector systems. Given the reliability of this source of energy, it is necessary the production of systems to take advantage of all solar radiation.

At present, low-temperature solar thermal systems (80–150 °C) are abundant and are usually used for domestic hot water production [1]. Besides the research works based on enhancing the thermal performance of the solar thermal collectors, there is also an interest on increasing reliability and long-term performance stability of these collectors [2,3].

In a solar collector, the most important component is the absorber due to its surprising aptitude to collect the energy in sunlight and transform the incident solar irradiation into heat suppressing heat losses on account of thermal radiation [4,5]. It has to satisfy two conditions: a high value of absorptance of the solar irradiation in the solar wavelength range (0.3–2.5 μm) and a low value of thermal emittance in the mid/far-infrared wavelength ranges (> 2.5 μm) [6,7]. However, no single material in nature can meet these requirements. Therefore, it is required an optimization of the optical and structural properties of the surface to achieve the desired wavelength selectivity. For that, it is necessary the use of a combination of materials, the modification of its surface or the synthesis of multilayer solar absorber materials [8]. For this reason, a lot of effort has been directed in the preparation of new selective absorbers for solar collectors increasing thereby the interest in solar absorber coatings. In fact, the more efficient the absorber, the greater the collector's output.

There are different techniques for the optical coatings deposition: vacuum techniques (CVD and sputtering) and soft chemistry techniques as dip-coating. The last technique is based on the immersion of the substrate into a solution and extracting it at a constant rate. The solutions used may be prepared from metal alkoxides (sol-gel technology) or also from metallic inorganic salts. Once the solution is deposited on the substrate, the sample is subjected to a thermal treatment to obtain the corresponding oxide. In fact, the sintering temperature and the duration of this thermal treatment, among other variables, are critical in the preparation of a competent selective absorber by dip-coating because it can influence its properties as well as its structural characteristics [9]. Nowadays the dip-coating method is widely used due to its singular characteristics such as cost-effectiveness, simplicity and reproducibility [10]. By applying this technique, parameters as the solution concentration, the withdrawal speed and the drying time can be controlled. Consequently, some parameters as morphology, uniformity and thickness of the films can be tuned [11].

Usually, selective absorber coatings are applied onto metal substrates (Cu, Al, steel) due to their appealing properties such as corrosion resistance, low thermal emittance and high thermal conductivity [12,13].

Recently, the spinel-type transition metal oxides are acquiring

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special interest in the field of solar energy conversion [14]. Among the multiple coatings composed of transition metal oxides with spinel-like structure, copper-manganese oxide ($CuMnO_x$) has been found to be a selective absorber with the necessary optical and structural characteristics [15–17]. The optimization of this absorber has allowed to reach yields superior to those available commercially, being therefore interesting its application in low-temperature solar thermal systems, as it is demonstrated in this paper.

2. Experimental

The $CuMnO_x$ and $FeMnCuO_x$ solutions were prepared from copper nitrate (Sigma Aldrich, 98–103%), manganese nitrate (Panreac, 97%) and iron nitrate (PRS Panreac, 98%) dissolved in absolute ethanol. The molar ratio in the precursors for $CuMnO_x$ was 1:1 and for $FeMnCuO_x$ was 1:1:2. In these precursor alcoholic solutions, a complexing agent and a wetting additive were added improving in this way the adhesion of the films [18]. The SiO_2 solution was prepared via sol-gel chemistry and Tetraethylortosilicate (TEOS) was used as precursor. This compound was mixed with distilled water and ethanol and hydrochloric acid as catalyst. The molar ratio TEOS:ethanol:water was 1:18:5.

A scheme of the three layers configuration studied as selective absorber is presented in Fig. 1. It consists of a first layer of $CuMnO_x$, a second layer of $FeMnCuO_x$ and a third layer of SiO_2.

$CuMnO_x$ films were deposited on aluminum by dip-coating at 22 °C at different withdrawal rates (36–46 cm/min) and sintered at 600 °C. Afterward, on this first layer, $FeMnCuO_x$ and SiO_2 antireflective coatings were deposited separately following the same procedure explained above.

The hemispherical reflectance spectra of the samples were measured from 0.3 to 2.5 µm by using a UV–VIS–NIR Perkin-Elmer LAMBDA 950 double beam spectrophotometer equipped with a 150 mm Spectralon® coated integrating sphere. The measurement uncertainty associated was 1%. Solar absorptance (α_s) was calculated according to standard procedure [19] and using the direct AM1.5 solar spectrum from ASTM G173-03 [20] between 0.3 and 2.5 µm, applying the following equation

$$\alpha_s([0.3,\ 2.5],\ \theta_i,\ T_s) = \frac{\int_{0.3}^{2.5} [\alpha_\lambda(\lambda,\ \theta_i,\ T_s)] G_b(\lambda) d\lambda}{\int_{0.3}^{2.5} G_b(\lambda) d\lambda} \quad (1)$$

Where

α_s (λ, θ_i, T_s) is the spectral absorptance, calculated from $1-\rho_\lambda(\lambda)$ being $\rho_\lambda(\lambda)$ the spectral hemispherical reflectance measured in the spectrophotometer G_b (λ) is the spectral solar irradiance.

Similarly, the aluminum solar reflectance (ρ_s) was calculated by weighting the spectral hemispherical reflectance measured in the spectrophotometer with the AM1.5 solar spectrum.

Besides solar absorption, samples thermal emittance (ε_T) was also obtained by using a Perkin Elmer Frontier FTIR spectrophotometer equipped with a diffuse gold-coated integrating sphere. The measurement uncertainty associated was 2%. Thermal emittance was calculated from the hemispherical IR-reflectance spectra recorded from 2.5 to 17 µm at room temperature and the black body spectrum for 100 °C, applying the following equation:

$$\varepsilon_T = \frac{\int_{2.5}^{17} [1-\rho_\lambda(\lambda)] i_{\lambda,\ bb}(\lambda,\ Ts) d\lambda}{\int_{2.5}^{17} i_{\lambda,\ bb}(\lambda,\ Ts) d\lambda} \quad (2)$$

Where

$\rho_\lambda(\lambda)$ is the spectral hemispherical reflectance measured in the spectrophotometer

$i_{\lambda,bb}$ is the emission intensity of a black body for every wavelength at a given temperature, calculated according to Planck's law.

An optical microscope Leica DM4 M was used to study layers morphology and a profilometer Bruker's DektakXT™ Stylus Profiler was used to determine the thickness of the different layers. Concretely, a stylus type of 2 µm was used and a force of 6 mg was applied to perform the measurements.

3. Results and discussion

Reflectance of aluminum in the solar spectrum is very high in comparison with any other metal substrate. But, it is well known that a native aluminum oxide film is formed spontaneously on its surface when it is in air at room temperature [21]. This native layer protects the metal from corrosion but it can also affect the optical reflectance. Moreover, this layer can avoid the homogeneous coating deposition on it.

In this way, the effect of a chemical etching with a 5% HF solution to remove the alumina layer on aluminum substrate has been tested. Different times of etching between 10 and 60 s were checked and the effects in the hemispherical reflectance spectra were studied. In Fig. 2 it is shown the hemispherical reflectance spectrum of an aluminum substrate as received and the hemispherical reflectance spectra of aluminum substrates etched during 10, 30, 45 and 60 s. As it can be seen, reflectance is increased after the etching step, being the solar reflectance value obtained for the etched sample of 0.90 meanwhile the value for the as received sample is 0.84.

No variations in the hemispherical reflectance spectra were obtained by using longer etching times, demonstrating that 10 s are enough to remove completely the alumina layer. In addition, it has been observed that after this chemical etching, the homogenous deposition of the coatings on the aluminum substrate is favored. Fig. 3 shows photographs of $CuMnO_x$ coated samples deposited at a withdrawal rate of 42 cm/min on the aluminum etched during 10 s in a 5% HF solution (a) and on the aluminum as received (b). It can be observed that the coating on the etched sample is homogeneous, and only variations referred to the border effect are seen. On the contrary, the sample

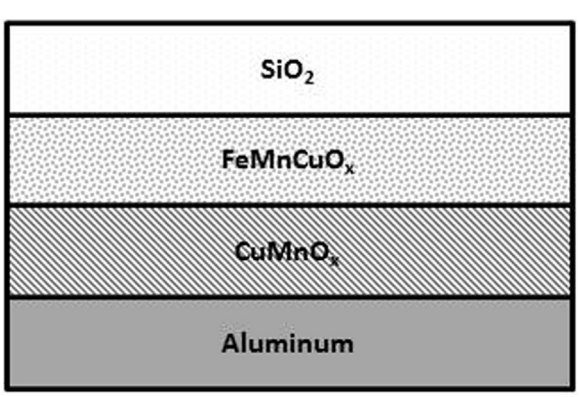

Fig. 1. Scheme of the three layer configuration of the presented selective absorber.

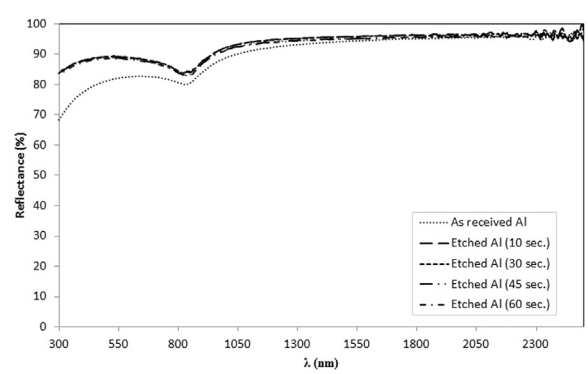

Fig. 2. Hemispherical reflectance spectra of as received aluminum substrate and etched aluminum substrates during 10, 30, 45 and 60 s.