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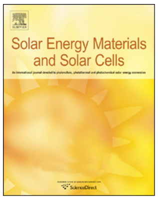

First spectral emissivity study of a solar selective coating in the 150–600 °C temperature range

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ABSTRACT

A complete experimental study of temperature dependence of the total spectral emissivity has been performed, for the first time, for absorber–reflector selective coatings used in concentrated solar power (CSP) systems for energy harvesting. The coating consist of double cermet layers of silicon oxide with different amounts of molybdenum over a silver infrared mirror layer. The experimental measurements were carried out by a high accurate radiometer (HAIRL) with controlled atmosphere in the mid-infrared and for temperatures between 150 and 600 °C. The spectral emissivity is nearly constant in this temperature range. Therefore, the temperature dependence of the total emissivity is given by Planck function. These results were compared with those obtained with the usual calculus using room temperature reflectance spectrum. Finally, the performance of the coating was analyzed by comparison of coated respect to non-coated stainless steel.

1. Introduction

Solar thermal devices are an alternative to produce heat from the sun for heating systems ($T < 150$ °C) and also to produce solar thermal electricity ($150\ °C < T < 800\ °C$). In these devices both, the thermal energy storage and the solar thermal collectors (STC) with different configurations (i.e. flat-plate collector and parabolic concentrated collector), have special relevance. In the case of STCs, the solar absorber surface (SAS) is the most important part. A surface that facilitates the conversion of solar radiation into useful heat should possess two important properties: to absorb the incoming solar radiation as much as possible (i.e. high solar absorptivity, α, at the vis–NIR wavelengths) and, at the same time, to retain the collected heat (high thermal reflectivity, R, or low emissivity, ε, at NIR–MIR region [1]).

The most common type of absorber is based on materials which are black in the solar radiation range but transparent for the heat, like metal–ceramic nano-composites ("cermets"). Among all the existing mechanisms, an absorber–reflector tandem consisting of small transition metal particles embedded in a dielectric matrix deposited on a highly infrared reflecting substrate is the most suited method. These thin film coatings offers a high degree of flexibility in order to obtain the desired optical properties to achieve the expected solar selectivity values by changing the thickness, metal volume fraction, and the shape of metal nano particles [2].

Currently, most of the commercial SAS are prepared by magnetron sputtering technology that is a dry, clean and eco-friendly process allowing large area deposition as compared to the electrochemical methods [3–6]. These SASs are composed of two or four homogeneous cermet layers with different metal contents or one cermet layer with a graded refractive index [7,8]. The selectivity can be increased adding more layers [9] but, in this case, the price increases and durability decreases [10], being the double layer cermets the base for the most successful solar selective coatings for medium-high temperature applications [11–14].

Generally the tandem absorbers are degraded at high operating temperatures due to their unstable microstructure, which cause a decrease in the solar selectivity (defined as α/ε). One of the essential requirements of solar selective absorbers is their stability when they operate at high temperatures, from approximately 400 to 600 °C. Optical properties of these coatings should not deteriorate with the rise of the temperature during the period of use.

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To accomplish this, new more efficient selective coatings are needed to get both high solar absorptivity ($\alpha > 0.96$) and low thermal emittance ($\varepsilon < 0.05$) at the working temperature range (400–600 °C). In fact, for high temperature applications, low ε is the key parameter, because the thermal radiative losses of the absorbers increase proportionally to T^4 [15].

In order to analyze heat losses, a complete knowledge of the radiative properties of the coating structure is essential for their use in high temperature solar collectors. However, a systematic study of direct total spectral emissivity as a function of the temperature for homogeneous cermet of two layers has not been performed yet. For instance, all the measurements reported in the literature were carried out at room temperature or, at most, at 100 °C. Therefore, the values of emissivity at working temperatures (400–600 °C) are obtained by extrapolation, which can introduce significant errors in the final result.

This study is focused on the relevance of the high temperature radiometric emissivity techniques in the optical characterization of the SAS. In this paper this experimental technique is applied to study the spectral emissivity behaviour of a coating with double layer cermets of silicon oxide with different amounts of metal. The measurements were carried out using a high accurate radiometer with controlled atmosphere in the medium infrared range and for temperatures between 150 and 600 °C. The results obtained in this study are compared to those obtained with indirect methods.

2. Experimental

2×2 cm^2 plates of stainless steel AISI-321 were used as substrates for the coatings. The substrate roughness was measured using a commercial rugosimeter and the obtained values are showed in Table 1, where R_a is the roughness average, R_z the average maximum height and R_t the maximum height of the profile.

The selective solar coating was prepared by sequential sputtering deposition on steel substrate, air-annealed during 2 h to develop a thermally grown oxide barrier layer. High purity silver, and molybdenum targets were sputtered with Ar gas at 5×10^{-3} mbar with RF and DC powers of than 25 W and 1 W to obtain deposition rates of 10 and 1.7 nm min^{-1} respectively. Moreover, pure silicon target was also sputtered with a 10% O_2/Ar gas mixture at 5×10^{-3} mbar by applying a RF power of 100 W to form silicon oxide layers with a deposition rate of 7 nm min^{-1}. The selective solar coating, prepared using these growing conditions, is schematically represented in Fig. 1. From the bottom, the deposited stack is formed by four layers: (i) 250 nm thick silver layer acting as IR-mirror, (ii) 85 nm thick layer of high metal volume fraction (HMVF) cermet composed by Mo and SiO_2 with 50% filling factor, (iii) 85 nm thick layer of low metal volume fraction (LMVF) cermet composed by Mo and SiO_2 with 20% filling factor and, on top, (iv) 53 nm thick antireflective layer of SiO_2.

Table 1
Sample surface roughness.

R_a (μm)	R_z (μm)	R_t (μm)
0.13	0.87	2.14

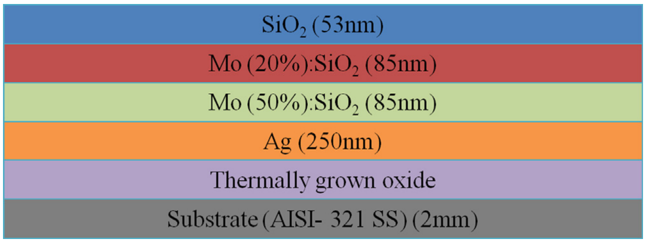

Fig. 1. Schematic representation of the selective solar coating used for the emissivity characterization.

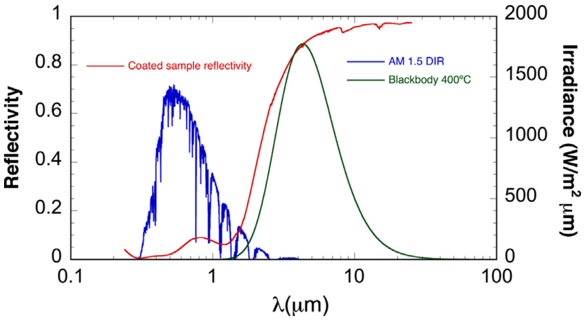

Fig. 2. UV–vis–IR reflectivity of the selective solar coating of Fig. 1.

Fig. 2 shows the measured reflectivity at the UV–vis–IR wavelength range to illustrate the selective character of such a multilayer coating. UV–vis–IR reflectivity measurements were performed using both a Shimadzu SolidSpec-3700 spectrophotometer, in the range of 0.19–3.30 μm, and a Varian 660-IR FTIR spectrometer in the 2.5–25 μm wavelength range. It can be easily observed the abrupt change in the reflectivity spectrum ($R(\lambda)$) from very low values at the UV–vis region to very high ones at the IR range, which makes possible to obtain a total solar absorptivity of $\alpha_S = 0.9$, and a total thermal emissivity at room temperature of $\varepsilon_{Th} = 0.02$. These values have been calculated by the well known expressions (1) and (2), using the measured near normal reflectivity $R(\lambda)$ in good approximation of the angle dependent $R(\lambda,\theta)$

$$\alpha_s = \frac{\int_0^\infty [1 - R(\lambda)] A(\lambda) d\lambda}{\int_0^\infty A(\lambda) d\lambda} \tag{1}$$

$$\varepsilon_T(T) = \frac{\int_0^\infty [1 - R(\lambda)] L(\lambda, T) d\lambda}{\int_0^\infty L(\lambda, T) d\lambda} \tag{2}$$

where $A(\lambda)$ is the Solar emission ASTM G173-03 Reference Spectrum (AM1.5) and $L(T, \lambda)$ the Planck function.

The spectral emissivity measurements were carried out using a high accuracy infrared radiometer (HAIRL) described in Ref. [16], which allows accurate signal detection and fast processing. A diaphragm adjusts the sample area viewed by the detector and ensures good temperature homogeneity of the sample measured area. The sample holder permits directional measurements, while the sample chamber ensures a controlled atmosphere (vacuum, inert gas or open atmosphere). The set-up calibration was carried out by using a modified two-temperature method [17] and the emissivity was obtained applying the blacksur method [18]. The combined standard uncertainty of this direct emissivity device was previously obtained from the analysis of all uncertainty sources [19]. For the measurements presented in this paper, the maximum combined standard uncertainty varies between 1% and 9% depending on wavelength and temperature, its average value being around 3.5%. The sample temperature is measured by means of two K-type thermocouple spot-welded on the sample surface out of the area viewed by the detector. Before placing the sample in the sample holder its surface is cleaned in an ultrasonic bath of acetone. Once the sample is introduced in the sample chamber, the measurements were carried out in a moderate vacuum or with a slightly reducing atmosphere in order to prevent the oxidation of the sample surface. The measurements are performed during five heating cycles between room temperature and nearly 700 °C. For each heating cycle the emissivity is measured at six or seven