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$MoSi_2$–Si_3N_4 absorber for high temperature solar selective coating

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ABSTRACT

A novel absorbing composite based on $MoSi_2$–Si_3N_4 has been investigated to be used in high temperature solar selective coating applications. Simulation of the reflectance from the complex dielectric permittivity of the components has allowed the optimization of its optical characteristics. The sputtering deposited whole multilayer stacks, formed by a metallic infrared reflector, a double absorber composite and an antireflective layer, show optical performances as good as those obtained from similar composites such as Mo–Si_3N_4 but with improved stability in moderate vacuum at temperatures up to 600 °C.

1. Introduction

Thermal conversion of solar energy is one of the simplest methods of harvesting renewable energy. Typically, it is carried out in concentrated solar power (CSP) systems that, in order to be effective, require covering the fluid-containing tubes with materials of high solar absorbance and low thermal emittance. This absorber coating has to preserve its optimum optical properties at temperatures as high as possible because efficiency increases with working temperature. Even if, nowadays, typical operation temperatures are 400–450 °C [1], a target temperature of 600–650 °C is desirable for improving conventional parabolic trough collector (PTC) systems. Physical vapor deposition (PVD) techniques (and specially sputtering) are very interesting here because of the precise control of layer thickness coatings over a large area, which is a fundamental parameter to achieve the required optical properties [2].

A good balance between performance and cost is obtained with solar selective coatings (SSC) composed of a multilayer [3–5] containing the following four layers: (i) an infrared reflective metallic layer (IR-mirror) placed close to the substrate, (ii) a high metal volume fraction (HMVF) composite, (iii) a low metal volume fraction (LMVF) composite layer, and (iv) an anti-reflective (AR) layer.

Recently, several examples of nitride-based (including nitride and oxynitride compounds) solar absorber materials have been reported: TiAlN/TiAlON [6,7], NbAlN/NbAlON [8,9], HfMoN/HfON [10] and TiAlCrN/TiAlN [11], CrMoN/CrON [12], and cermets as Al–Al_xO_y–AlN_x [13], Mo–AlN and W–AlN [14] and Mo–Si_3N_4 [15–17]). In the later cases, due to the progressive oxidation of the cermet metal in time, investigation of its possible degradation is important to be considered regarding its long-time operation.

On the other hand, $MoSi_2$ was proposed as the conductive component of $MoSi_2$–Al_2O_3 composite to be used as SSC [18] and, recently, studies of its preparation and optical properties have been reported [19,20]. In order to find superior novel materials to build high temperature stable SSCs and taking into account the chemical stability of both $MoSi_2$ and Si_3N_4, we have investigated for the first time the $MoSi_2$–Si_3N_4 system. Molybdenum disilicide presents excellent high temperature stability properties [21,22], which provides exceptional properties to bulk $MoSi_2$–Si_3N_4 composites [23].

In this paper, we report on SSCs based on the above described four layers architecture. Even if tungsten has been recently proposed for the IR-mirror metallic layer because of its thermal stability and anti-diffusion properties [24], we have selected silver in order to test the optimum achievable emissivity values. The absorber consists of a double layer of high and low semiconductor volume fractions of $MoSi_2$ semiconductor embedded in the Si_3N_4 ceramic ($MoSi_2$–Si_3N_4 composite). On top, a Si_3N_4 layer acts as the dielectric antireflective (AR) coating.

Along this work, the preparation procedure to deposit this absorber composite is reported and the optical properties of whole selective multilayer stacks are investigated by simulations, where

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layers thickness and filling factors have been varied to achieve the optimum optical selectivity at high temperatures.

A precise experimental control of composition and thickness of the individual component layers has led to optimized solar absorptivity and thermal emissivity for temperatures above 600 °C. Additionally, thermal stability under moderate vacuum conditions (1×10^{-3} mbar) has been studied.

2. Experimental

The tandem absorbers were deposited by magnetron sputtering at room temperature on stainless steel AISI-321 substrates (labeled as SSth because of the previous air-annealing at 600 °C to develop its thermally grown oxide anti-diffusion layer). The stack materials were: silver as metallic IR reflector, $MoSi_2/Si_3N_4$ composites as composite layers, and silicon nitride as AR layer. The base pressure was around 1×10^{-6} mbar. The Ag layer (100 nm thick) was deposited by direct current (DC) sputtering of Ag with Ar at 9×10^{-3} mbar at 15 W (deposition rate 5 nm/min). After Ag deposition, the Ag layer surface was passivated inside the chamber by flowing oxygen at a pressure of 5×10^{-2} mbar during 15 min [15].

$MoSi_2$–Si_3N_4 composites were prepared by sequential deposition of $MoSi_2$ and Si_3N_4 layers as in a hetero-structure way. $MoSi_2$ layers were obtained by co-sputtering of Si and Mo targets using Ar as sputtering gas at 7×10^{-3} mbar. This is a very interesting preparation procedure because these two targets might be enough to fabricate the whole selective stack if metallic Mo is selected as the IR-mirror.

The desired $MoSi_2$ stoichiometry was obtained by applying 28 W (DC) and 92 W (RF) to the Mo and Si targets, respectively, and using Ar as sputtering gas at 7×10^{-3} mbar. Si_3N_4 layers were deposited by radio-frequency (RF) sputtering of a Si target using N_2 as reactive gas at 7×10^{-3} mbar [25]. The $MoSi_2$ content in the hybrid system (or filling factor, FF, in the composite) to obtain the required HMVF and LMVF composite was adjusted by tuning the relative thickness of $MoSi_2$ and Si_3N_4 strata.

Energy dispersive analysis X-ray fluorescence (EDAX) data were collected from an EDAX Genesis XM2i analyzer coupled to a FEI NanoSEM Nova 230 field emission-scanning electron microscope (FE-SEM). Rutherford backscattering spectroscopy (RBS) was performed at the 5 MV HVEE Tandetron accelerator located at the Centro de Micro-Análisis de Materiales of the Universidad Autónoma de Madrid [26]. RBS experiments were performed with helium ions (α) of an energy close to 3.03 MeV. This energy provides a strong resonance in $^{16}O(\alpha,\alpha)^{16}O$ cross section leading to the enhancement by a factor of 22 in the oxygen detection compared with the Rutherford cross section [27].

By using the CODE (Coating Designer version 3.75) software for optical spectroscopy, developed by Theiss [28], we have performed the calculation of the reflectance of the whole selective coating stack. This software allows, among other parameters, the variation of the $MoSi_2$–Si_3N_4 ratio in the composites and the thickness of all the layers in order to optimize the coating architecture.

UV–vis–IR reflectance measurements were performed using both a Shimadzu SolidSpec-3700 spectrophotometer in the range of 190–2600 nm and a Varian 660-IR FTIR spectrometer in the 1.5–25 μm wavelength range.

3. Results and discussion

3.1. Simulation of optical properties

In this section, the optimization of the coating architecture is presented by using the simulation of the optical properties of the coatings from the commercial CODE software. For SSC, the reflectance spectrum appears as the simulation output, from which solar absorptivity (α_{Sol}) and thermal emissivity (ε_{th}) values can be obtained to evaluate the SSC as it has been described elsewhere [15].

CODE software uses the complex dielectric permittivity as input data (or complex refractive index) of each material the coating is made of. For an adequate optical characterization, the reflectivity spectrum should range from 200 nm to 25 μm. To obtain this output range, the input data have to cover the same extent. However, for many materials the complex dielectric permittivity, accessible in databases or reported in literature, does not cover such interval. The complex dielectric permittivity of a large list of simple materials has to be used here: Fe [29], Fe_2O_3 [28] and Cr_2O_3 [28] to account for the thermally treated stainless steel substrate, Ag [30,31] for the IR-mirror and Si_3N_4 [32,33] for AR layer. For all of them, the complex dielectric permittivity components were taken from the literature and extrapolated (if needed), as shown in Fig. 1. Additionally, the complex dielectric permittivity of the composite has been obtained, for each FF, from those of $MoSi_2$ [34] and Si_3N_4 by using the Bruggeman effective medium model [35] since percolation of the absorber is expected.

Optimization of SSCs is based on a high reflectance at the IR wavelengths and a low reflectance at the UV-visible wavelengths. The IR reflectance fully depends on the buried metal (metallic IR-mirror layer or substrate) and the absorptance at the UV–visible wavelengths depends on the composite optical absorption and on the optical interference caused from layers. Consequently, the reflectance calculation becomes very useful for finding the set of composites and AR layer thicknesses, which provides the best solar absorptivity and thermal emissivity values for a given system.

For instance, Fig. 2 exhibits the results using the CODE software for Ag/$MoSi_2$–Si_3N_4 SSCs on thermally treated AISI-321 stainless steel substrates with different thickness of both the HMVF and LMVF layers at fixed FF. Simulation shows how critical the layer thickness is to allocate the transition between low and high values of reflectance, which determines the optical characteristics as a function of the desired working temperature of the coating. The final structure of the SSC should take into account the working temperature, but in accordance with both insets of Fig. 2, a thickness in the range 50–60 nm for LMVF and HMVF composites seems to be the best compromise between absorptivity and emissivity.

Another interesting point is how the $MoSi_2$–Si_3N_4 absorber compares to similar composites. Fig. 3 shows the comparison of the reflectance simulated for one of the best architectures for selective stacks based on $MoSi_2$–Si_3N_4, Mo–Si_3N_4 and $MoSi_2$–Al_2O_3 composites, where silver is used as the IR-mirror for all of them and the antireflective layer is Si_3N_4 for the nitride based composites and Al_2O_3 for the former case. For comparison purposes, the multilayer stacks of these three systems were designed to have a reflectance of 50% for a wavelength of 2000 nm. This is the reason why the simulated reflectance spectra are so similar for these three systems. Nevertheless, Si_3N_4-based composites show better optical behavior in the 600–1200 nm range, evolving a better absorption of the solar radiation. This fact, together with the high temperature stability expected for the $MoSi_2$–Si_3N_4 composite makes the preparation of SSCs based on this system very interesting in order to asses its actual optical performance and its high temperature behavior.

3.2. $MoSi_2$–Si_3N_4 composite preparation

The optical properties of a SSC are determined by the complex refractive index of both composite components, which at the visible range, is mainly determined by the electronic density. On