



High-temperature air-stable solar selective coating based on $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composite



Adrián Rodríguez-Palomo, Eva Céspedes¹, David Hernández-Pinilla², Carlos Prieto*

Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

The thermal stability in air of solar selective coatings based on the novel $\text{MoSi}_2\text{-Si}_3\text{N}_4$ hybrid composite has been investigated here for the first time. Although thermal stability of solar absorbers is typically examined under vacuum, high temperature air stability is required for practical applications in concentration solar power (CSP) technologies: solar tower systems receivers operate in air and, on the other hand, air stability is highly preferred in parabolic trough collector systems due to occasionally undesired losses of vacuum conditions. In this work, the effect of different layers combination, prepared by sputtering, on the optical performance after high temperature annealing has been investigated. Two different standard substrates (stainless steel and Inconel) have been explored. It is shown that silver layer, typically used in SSC as IR reflector, strongly affects the stack thermal stability in air, leading to important degradation. For SSC stacks with the Inconel/ $\text{MoSi}_2\text{-Si}_3\text{N}_4\text{/Si}_3\text{N}_4$ structure (onto Inconel substrate), a good thermal stability in air is obtained, leading to just a slight variation of the absorptivity after air annealing at 600 °C, probably due to partial Si_3N_4 oxidation. Best optical performance is achieved for the Inconel substrate, using and additional Al_2O_3 barrier on top, comprising the stack the following structure: Inconel/ $\text{MoSi}_2\text{-Si}_3\text{N}_4\text{/Si}_3\text{N}_4\text{/Al}_2\text{O}_3$. This combination exhibits very good optical performance, even after annealing at 700 °C in air. The Performance Criterion (PC) according to the International Energy Agency, evaluated after successive air annealing cycles of 100 h at 600 °C, gets 0.02, which is considerably smaller than 0.05, fulfilling this material the PC for practical applications. Our results evidence that the $\text{MoSi}_2\text{-Si}_3\text{N}_4$ absorber deposited onto Inconel substrate and capped with a $\text{Si}_3\text{N}_4\text{/Al}_2\text{O}_3$ layer on top (acting as antireflective and protective barrier) is a very promising selective coating for solar receivers operating in air at temperatures about 600 °C.

1. Introduction

Solar selective coatings (SSC), typically prepared by physical vapor deposition techniques (PVD) [1], are important component of receivers in concentrated solar power (CSP) technology [2,3]. Their optical properties should remain suitable at temperatures as high as possible because efficiency increases with working temperature. Temperatures in the 600–650 °C range are required to improve efficiency of conventional parabolic trough collector (PTC) systems. The fact that collectors operate under vacuum (or inert gas) conditions has focused research on vacuum-stable coatings [4]. Nonetheless, air stability at high temperature is required for practical applications due to occasionally undesired losses of inert conditions. Additionally, receivers of high concentration solar tower systems work in air at temperatures near 800 °C, but the paints used in this technology have low difference between solar

absorptivity and thermal emissivity (and therefore lack of an adequate optical selectivity or efficiency). Consequently, actual temperatures at what stability in air is maintained and optical selectivity are nowadays two important parameters to be maximized for technological applications of CSP coatings.

The main strategy to improve selectivity is to obtain an appropriate figure of interference between layers forming the coating. By controlling the layers thickness and composition, it is possible to take advantage of the high reflectance of the metallic substrate (or metallic buried layer) at the infrared (IR) wavelength range and of the high absorbance of the so-called absorber material at the ultraviolet - visible (UV-Vis) region.

Absorbers based on cermets were first proposed by Granqvist and Niklasson [5], in which absorptivity becomes strongly improved by a double interference cermet structure [6]. A double cermet is composed

* Corresponding author.

E-mail address: cprieto@icmm.csic.es (C. Prieto).

¹ Present address: IMDEA Nanociencia, E-28049 Madrid, Spain.

² Present address: Dept. Física de Materiales, Universidad Autónoma de Madrid, E-28049 Madrid, Spain.

by two sublayers with a high metal volume fraction (HMFV) and a low metal volume fraction (LMVF) where a grade metal multilayer structure together with a ceramic anti-reflective (AR) layer on top and a metallic IR-mirror at the bottom, produce a gradually decrease of the refractive index (n) and extinction coefficient (k) [7]. Such a coating architecture enables excellent optical properties of the whole stack, being particularly useful to control selectivity since solar absorptivity and thermal emissivity for an operation temperature may be easily tuned by tailoring the layer thickness and/or the cermet metal volume fraction [8,9].

There are several combinations of metals and ceramic compounds reported in literature as possible candidates for cermet materials in the SSC stack [1,4]. Transition metals within oxides or nitrides are selected to form the cermet layers. Typically, for high temperature applications they have been formed by molybdenum or tungsten as the metallic part and silicon oxide or aluminum/silicon nitride as the ceramic one in Mo–SiO₂ [10], Mo–AlN and W–AlN [11], Al–Al_xO_y–AlN_x [12], Al–AlN [13] and Mo–Si₃N₄ [14] systems that effectively compete on cost with Pt–Al₂O₃ [15]. Other similar combinations are hybrid composites in which metals are substituted by stable semiconductor compounds as in MoSi₂–Al₂O₃ [15–17] and MoSi₂–Si₃N₄ [18].

The emerging solar industry field is demanding reliable coatings able to keep their optical and chemical properties over a long operational lifetime. Nowadays there are not available selective coatings on the market capable of high temperature performance in air, showing a drastic reduction of their lifetime because of their strong reactivity when exposed to atmospheric oxygen. Furthermore, commercial coatings are just placed on the collector surface using spraying or brushing [19]. To date, Piromark-2500 (with near-normal solar absorbance ~ 0.97 only for a short time and thermal emissivity from ~ 0.8 at 100 °C to ~ 0.9 at 1000 °C) is the commercially used reference for high temperature tower receivers [20]. These black protective paints have low selectivity ratio, with high emissivity values which result in large radiative heat losses [21]. In this line, available commercial products do not have the required selectivity to face the problem of thermal losses.

Several studies dealing with the thermal stability of solar selective coatings have been published, being the highest temperature without degradation in air about 500 °C. The best stability in air was obtained using a single layer cermet made of Ni–Al₂O₃ covered with a SiO₂ antireflective layer ($\alpha_{\text{sol}} = 0.84$ and $\epsilon_{\text{th}} = 0.07$ at 100 °C) [22]. This multilayer structure prepared by sputtering showed stability of its optical properties up to 500 °C for 1000 h. However, a slight increase of temperature up to 550 °C lead to a dramatic degradation of the coating [23]. More interesting is the stability reported for the Mo–SiO₂ based SSC after air-annealing at 450 °C after 3000 h [24]. Among the investigated materials, one of the largest absorbance was reached with (Al_xO_y–Al–Al_xO_y)-based SSC with an absorptivity and emissivity values of 0.97 and 0.08 at 85 °C [25]. Nonetheless, this combination led to an extremely poor stability at 400 °C in air, being their properties degraded after just two hours. Other combinations have been tested in air at higher temperatures; for instance, stability of TiAl/TiAlN/TiAlON/TiAlO has been reported at 500 °C for one hour [26], TiAlN/TiAlON/Si₃N₄ at 600 °C for two hours [26] and SS/Mo/AlCrON/AlCrO_x at 600 °C for 168 h [27] (SS stands for the stainless steel substrate).

In previous works we have reported the vacuum stability of SS/Ag/Mo–Si₃N₄/Si₃N₄ stacks at 600 °C (with ($\alpha_{\text{sol}} = 0.93$ and $\epsilon_{\text{RT}} = 0.02$ and $\epsilon_{600\text{ °C}} = 0.11$) [14], with comparable optical performance when the absorber is substituted by the MoSi₂–Si₃N₄ hybrid composite (with ($\alpha_{\text{sol}} = 0.88$ and $\epsilon_{\text{RT}} = 0.02$ and $\epsilon_{600\text{ °C}} = 0.11$ values) [18] but improved thermal stability in vacuum. Highly stable optical properties under vacuum annealing at 600 °C during more than 200 h have been reported [28] for this latter SS/Ag/MoSi₂–Si₃N₄/Si₃N₄ stack architecture. The SSC optical behavior after vacuum annealing evidences that no reactivity occurs between the material components. Nevertheless, air annealing adds additional issues, mainly related to possible oxidation of the different components. Two specific effects on SSCs have to be

considered, one is the possible degradation of the IR-mirror (i.e. oxidation) layer and the other one is related to the composition modification of the absorber and AR-layers.

The aim of the present work is to report on high temperature air stable SSC stacks based on the barely explored MoSi₂–Si₃N₄ hybrid composite absorber and the Al₂O₃ antireflective layer, which acts also as operative barrier against oxidation. Due to the key effect of the substrate on the thermal stability of the system (because of diffusion of elements from the alloy), and being as faithful as possible with the industrial design, only stainless steel (SS) and Inconel® substrates have been considered.

2. Experimental

Using a base pressure around 1×10^{-6} mbar, SSCs were prepared by magnetron sputtering at room temperature on stainless steel AISI-321 and Inconel®–625 substrates (from Goodfellow with references FE210380 and NI043026, respectively). Substrates were cleaned with acetone and isopropyl alcohol and no additional polishing was applied. Its roughness was measured by profilometry over ranges larger than 1.5 mm, the obtained root mean square values were always $R_a < 0.2 \mu\text{m}$ for both types of substrates. In order to form an anti-diffusion thermally growth oxide, stainless steel substrates were annealed at 600 °C during 2 h in air (SS_{th}).

MoSi₂–Si₃N₄ absorber composites were prepared by sequential deposition of MoSi₂ and Si₃N₄ layers as in a hetero-structure way. MoSi₂ layers were obtained by co-sputtering of Si and Mo targets using Ar as sputtering gas at 7×10^{-3} mbar. Si₃N₄ layers were deposited by radio-frequency (RF) sputtering of a Si target using N₂ as reactive gas at 7×10^{-3} mbar. The MoSi₂ content in the absorber (filling factor, FF) to obtain the required HMFV and LMVF composite was adjusted by tuning the relative thickness of MoSi₂ and Si₃N₄ layers. Finally, Al₂O₃ antireflective layer was deposited from an Al₂O₃ target by using Ar as sputtering gas. Evaluation of the layer composition is made by using the calibration performed by Rutherford Backscattering Spectroscopy (RBS) and scanning electron microscopy - energy-dispersive X-ray spectroscopy (SEM-EDS), details have been given elsewhere [18]. Deposition thickness rate calibration and substrate roughness measurements were made by a Veeco Dektak 150 profilometer.

Air annealing was performed in a temperature controlled tubular furnace during periods of 15 h to characterize the temperature effect and during periods of 100 h to study the annealing for long times, using 2 °C/min ramps were used and cooling. Samples were placed in a quartz tube, which is opened to air from the two sides without forced circulation. No special control or characterization was made to that laboratory air.

SSCs were characterized by optical spectroscopy in reflectance mode using a Shimadzu SolidSpec-3700 UV–VIS–NIR spectrophotometer equipped with an integrating sphere and a Varian 660-IR FTIR spectrometer with a KBr interferometer. BaSO₄ and Au samples were measured as 100% reflectance standards for the 0.25–0.8 μm and 0.8–30 μm ranges, respectively.

By using the CODE (Coating Designer version 3.75) software for optical spectroscopy, developed by W. Theiss [29], prior to deposition we have performed the simulation of the reflectance of the whole selective coating stack in order to have some approximate values of FF (MoSi₂–Si₃N₄ ratio) and layer thickness that optimizes the coating structure.

3. Results and discussion

Table 1 summarizes the structure of the SSC stacks studied in this work and the relevant optical parameters of the “as-prepared” samples. Sample labeling is made to keep in mind the multilayer structure by using “S”, “I”, “SN” and “ALO” to refer to thermally treated stainless steel (SS_{th}), Inconel-625, “Si₃N₄” and “Al₂O₃”, respectively; and “H” to

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