Surface & Coatings Technology 284 (2015) 31–37

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Design, properties and degradation mechanisms of Pt-Al_2O_3 multilayer coating for high temperature solar thermal applications

Carine Gremion [a,*], Christian Seassal [b], Emmanuel Drouard [b], Arnaud Gerthoffer [a], Nathalie Pelissier [a], Cedric Ducros [a]

[a] *CEA, LITEN, F-38054 Grenoble, France*

[b] *Université de Lyon, Institut des Nanotechnologies de Lyon (INL), UMR CNRS 5270 École Centrale de Lyon, 36 avenue Guy de Collongue, F-69134 Écully Cedex, France*

ARTICLE INFO

Article history:
Received 17 April 2015
Revised 12 August 2015
Accepted in revised form 12 August 2015
Available online 5 September 2015

Keywords:
Solar thermal absorbers
Multilayer coating
Selective absorber
Platinum
Alumina
Thermal aging
Aging tests

ABSTRACT

Thin film composite materials, especially alumina-platinum (Al_2O_3-Pt) multilayer coatings, are promising materials for Concentrated Solar Power (CSP) applications, because of their good resistance to heat and oxidation. In this paper, we will present our work on the design and realization of such coatings. Our absorbers are composed of a substrate (Si, stainless steel and Inconel), a metallic infrared (IR) reflector and an alternation of thin Al_2O_3 and Pt layers. The absorber structure was optimized by optical simulations and then we used magnetron sputtering to deposit these coatings on different substrates. Then we made optical characterization, transmission electron microscopy (TEM) and chemical characterization to study these coating as deposited and after thermal aging at 650 °C in air. By using different kinds of IR reflector (molybdenum (Mo) reflector, Pt reflector or no reflector) we demonstrate that the choice of this layer is of great importance for the stability of the whole absorber. We show that Mo reflector is not suitable for applications at high temperature in air. Best results were obtained with a 7 layer stack, comprising a Pt reflector. A solar absorption of $\alpha = 0.93$ and a thermal emissivity of $\varepsilon = 0.43$ (calculated for a temperature of 650 °C) were achieved after aging at a constant temperature of 650 °C in air during 100 h.

1. Introduction

Solar energy harvesting is a promising way to provide carbon free energy in the future. One way to harvest such energy can be solar thermal power systems, which unlike photovoltaic cells, convert solar energy into heat and don't use the photoelectrical effect. The produced heat can be used in industrial processes implying heating or in thermal power stations.

To convert efficiently solar energy to heat, a good optical selectivity is required, i.e. an absorption as close as 100% in the visible range and an emissivity as close as 0% in the infrared (IR) range [1]. It can also be expressed in terms of reflectivity with a reflectivity close to 0% in the visible range and close to 100% in the IR range. The transition between these two wavelength ranges depends on the working temperature of the absorber, as it defined the intrinsic emissivity of the material, and is usually comprised between 1.5 and 2 μm in wavelength. Very few materials have good intrinsic selectivity, which means we need to engineer them to achieve the desired optical properties. The most commonly used absorbers are black paints, but they can't withstand temperatures higher than 200 °C. Recent studies focused on cermet (ceramic metal composites) or multilayer structures because they can benefit from the thermal stability and transparency of the ceramic and the high absorption of metals [2].

Attaining high temperature is also a key issue of thermal solar power. Nowadays, commercial solutions can operate around 300 to 500 °C and need a vacuum environment, because of the high oxidation or diffusion rate of the used materials at higher temperature [3]. For example, it's the case of molybdenum (Mo)–silica (SiO_2) metal–ceramic composite (or cermet), where the Mo particles imbedded in the SiO_2 matrix tend to oxidize rapidly in air. But, to be cost effective, solar thermal power needs to operate at temperature higher than 600 °C, to enhance the conversion yield of the thermal energy into electricity via Carnot heat engine. It must also be able to work in air to avoid the cost of the vacuum tube. This requires working with materials which can withstand such high temperature and are chemically stable for more than 20 years.

Noble metals are a good choice for this application, because of their good resistance to oxidation and their metallic optical behavior, especially platinum (Pt) due to its high melting temperature (2041.3 K) [4]. Many absorbers were made with cermet composed of an alumina (Al_2O_3) matrix containing metal particles, because of Al_2O_3 resistance to oxidation and thermal stability. For example, Thornton et al. [5] deposited Pt-Al_2O_3 cermet on different IR reflector materials and studied

---

[*] Corresponding author at: CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.
E-mail address: carine.gremion@cea.fr (C. Gremion).

http://dx.doi.org/10.1016/j.surfcoat.2015.08.076

resistance to aging at temperatures ranging from 300 °C to 600 °C for 150 h. If the absorption varied of more than 2%, it was considered that the absorber had failed, but the authors have not analyzed their samples to understand the degradation mechanisms. More recently, Nuru et al. [6] studied the thermal stability of a three layer structure made of a 7 nm Pt layer between to Al_2O_3 layers on a copper (Cu) substrate. They showed that, for temperatures of 600 °C and higher, the Cu from the substrate diffused in the absorber to the surface and degraded the optical properties of the absorber. The Cu diffusion effect was so strong that it overshadowed every other possible mechanisms. These studies highlight the need for more precise understanding of the degradation mechanisms taking place in a Pt-Al_2O_3 based absorber, to be able to avoid this degradation or, at least, reduce it.

In this study, we optimized and deposited a solar selective absorber, based on a Pt-Al_2O_3 multilayer structure. We used optical simulation to optimize our absorber absorption and emissivity. Pt-Al_2O_3 multilayers were realized by magnetron sputtering. We used transmission electron microscopy (TEM) imaging to study the impact of the Pt layer thickness on the morphology of this layer and Glow Discharge Spectroscopy (GDS) to analyze the chemical composition of our structure. Reflectance spectra were measured to study the optical properties of our coatings. We also investigated the influence of the IR reflector material on the optical properties of the coating, by realizing absorbers with IR reflector materials such as molybdenum (Mo), Pt or no IR reflector layer. The impact of the IR reflector material on the thermal stability of the absorber was studied by measuring the evolution of the optical properties during aging at 650 °C.

2. Materials and methods

First of all, we used an optical optimization program, called Optilayer, to determine the best multilayer configuration.

The Fig. 1 represents the two main designs of structures, optimized and realized in our study. The three layer structure presented on Fig. 1a) was used to study the morphology of the Pt layers depending on their thickness and the chemical composition of the layers. Fig. 1b) represents the complete absorber structure we designed. We used a needle optimization software program, called Optilayer, to determine the best number of layers and the best layer thickness, for our needs. We fixed a target reflectance value of 0% of reflectance between 300 nm and 1700 nm to the program, because the absorption is more critical than the emissivity in term of overall performance of the system [7]. We also implemented the basic structure and materials we wanted to use and Optilayer gave us the best number of layers and the best thickness for each layer to fit the reflectance target. We started with a structure composed of a Si substrate, an IR reflector layer, an Al_2O_3 layer, a Pt layer and another Al_2O_3 layer and we defined thickness ranges for each layer. Then the program calculated the best thickness for each layer to fit the specified target the most accurately. The simulation program repeated the same operation for a 2 Pt layers structure, a 3 Pt layers structures and so on, until we stop the calculation. It must be taken into account that our simulations are done with the hypothesis that our layers are continuous.

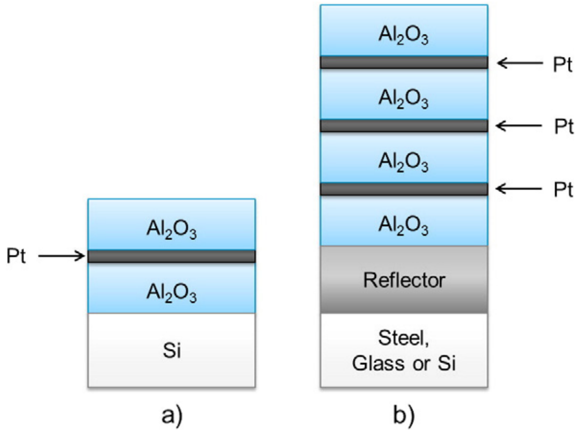

Fig. 1. Diagram of the different structures used in this study: a) three-layer structure and b) multilayer structure.

Then, the optimized structures were deposited on 25 × 25 mm^2 Si (100) substrates and on 25 × 25 mm^2 glass substrates for the three layers structure and the Pt IR reflector structure and additionally on 45 × 45 mm^2 316 stainless steel (SS) substrates for the structure with no reflector or Mo reflector. Before deposition, the substrates were washed using a cleaning equipment. The Mo reflective layer was deposited by direct current (DC) magnetron sputtering of a Mo target. The Pt layer deposition was made by DC-pulsed sputtering of a Pt target in an Ar atmosphere and the Al_2O_3 layer deposition was realized by reactive sputtering of an Al target in a mixt O_2-Ar atmosphere (11% O_2, 89% Ar). We measure the poisoning of the Al target to select our condition of deposition. The multilayer structure was obtained by sliding the substrate holder in front of the Pt or Al target alternatively. The deposition rate was approximately 14.9 nm/min for the Pt and 8.7 nm/min for the Al_2O_3. The pressure in the chamber was $5.4 \cdot 10^{-3}$ mbar for the Pt and $4{,}5.10^{-3}$ mbar for the Al_2O_3. We used a power of 200 W on the Pt target and 600 W on the Al_2O_3 target.

The optical measurements were realized in the UV–visible range (250–2500 nm) with a Perkin-Elmer Lambda 950 spectrophotometer and in the IR range (2500–20,000 nm) with a Bruker Equinox 55 spectrophotometer. In both cases, we made our measurements with an integrating sphere. After these measurements, we calculated the absorption and emissivity of each sample according to the following equations, given by Arancibia-Bulnes et al. [8]:

$$\alpha = \frac{\int_{2000}^{300} (1 - R(\lambda)) \times \Phi(\lambda) d\lambda}{\int_{2000}^{300} \Phi(\lambda) d\lambda} \tag{1}$$

$$\varepsilon = \frac{\int_{20000}^{2000} (1 - R(\lambda)) \times \varepsilon_0 (T, \lambda) d\lambda}{\int_{20000}^{2000} \varepsilon_0 (T, \lambda) d\lambda} \tag{2}$$

where α is the absorption, ε is the emissivity, R the reflectivity, λ the wavelength, Φ the solar energy as a function of the wavelength and ε_0 the black body radiation as a function of the wavelength for a chosen temperature. In this study, we chose a temperature of 650 °C, which was the temperature used for our aging tests.

TEM images were realized with a JEOL 2000FX and a JEOL 3010 for the high resolution images. Energy Dispersive X-ray Spectroscopy (EDS) was also performed during TEM imaging. The samples for the top view images were deposited on copper grids. Those for the cross-section were deposited on Si substrates, and then pieces were cleaved and bonded face to face. The obtained structure was thinned in the middle by Focus Ion Beam until it was thin enough for TEM imaging.

Glow Discharge Spectroscopy (GDS) analysis were performed with an Horiba GD Profiler 2.

The aging tests were realized in a resistive heating furnace, in ambient atmosphere. The samples were heated at a rate of 200 °C/h until they reached the temperature of 650 °C. After the desired aging time, the furnace was left to cool without any applied cooling rate, for 30 h.

3. Results and discussion

3.1. Simulation results

Needle optimization enables us to rapidly test several configurations with different numbers of layers. In order to do this, we implement the basic structure and materials we want to use and Optilayer gives us the best number of layers and the best thickness for each layer to fit the reflectance target. The results are summarized in Table 1 and they