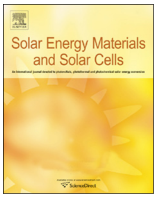
Solar Energy Materials and Solar Cells 185 (2018) 183–191

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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



Design of high-temperature solar-selective coatings based on aluminium titanium oxynitrides $Al_yTi_{1-y}(O_xN_{1-x})$. Part 2: Experimental validation and durability tests at high temperature

R. Escobar-Galindo[a,*], E. Guillén[b], I. Heras[c], G. Rincón-Llorente[d], M. Alcón-Camas[e], F. Lungwitz[f], F. Munnik[f], E. Schumann[f], I. Azkona[g], M. Krause[f]

[a] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, IMEYMAT, Universidad de Cádiz, 11510 Puerto Real, Spain*
[b] *Functional Surfaces and Nanostructures, Profactor GmbH, Im Stadtgut A2, 4407 Steyr-Gleink, Austria*
[c] *Department of Applied Physics, University of Salamanca, 37008 Salamanca, Spain*
[d] *IK4-TEKNIKER, Iñaki Goenaga street, 20600 Eibar, Gipuzkoa, Spain*
[e] *Abengoa Research S. L., Abengoa, Seville, Campus Palmas Altas 41014, Spain*
[f] *Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstrasse 400, 01328 Dresden, Germany*
[g] *Metal Estalki S.L., Polígono Ugaldeguren II, 48170 Zamudio, Spain*

ARTICLE INFO

Keywords:
Solar selective coatings
Thermal stability
Optical properties
Concentrated solar power
Optical simulation
Oxynitrides

ABSTRACT

The durability of two solar-selective aluminium titanium oxynitride multilayer coatings was studied under conditions simulating realistic operation of central receiver power plants. The coatings were deposited by cathodic vacuum arc applying an optimized design concept for complete solar-selective coating (SSC) stacks. Compositional, structural and optical characterization of initial and final stacks was performed by scanning electron microscopy, elastic recoil detection, UV–Vis–NIR-IR spectrophotometry and X-Ray diffraction. The design concept of the solar selective coatings was validated by an excellent agreement between simulated and initial experimental stacking order, composition and optical properties.

Both SSC stacks were stable in single stage tests of 12 h at 650 °C. At 800 °C, they underwent a structural transformation by full oxidation and they lost their solar selectivity. During cyclic durability tests, multilayer 1, comprised of TiN, $Al_{.64}Ti_{.36}N$ and an $Al_{1.37}Ti_{.54}O$ top layer, fulfilled the performance criterion (PC) ≤ 5% for 300 symmetric, 3 h long cycles at 600 °C in air. Multilayer 2, which was constituted of four $Al_yTi_{1-y}(O_xN_{1-x})$ layers, met the performance criterion for 250 cycles (750 h), but was more sensitive to these harsh conditions. With regard to the degradation mechanisms, the coarser microstructure of multilayer 1 is more resistant against oxidation than multilayer 2 with its graded oxygen content. These results confirm that the designed SSCs based on $Al_yTi_{1-y}(O_xN_{1-x})$ materials withstand breakdown at 600 °C in air. Therefore, they can be an exciting candidate material for concentrated solar power applications at high temperature.

1. Introduction

An optimal solar selective coating (SSC) to be used for central receivers in a concentrated solar power (CSP) plant needs to show appropriate optical properties as well as thermal and mechanical stability in air at high temperatures. In particular, coatings applied to central receivers do suffer thermal cycling during plant start-up and stop-down (plant handling) and thermal shocks during cloud transients. Despite the fact that the market of solar absorbers is rapidly increasing [1], a standardization for the service life prediction is still lacking, in particular for high temperature solar absorber coatings. In the 90's, the International Energy Agency (IEA) in Task X of the Solar Heating and Cooling (SHC) program developed a procedure to simulate the expected service lifetime of the coating over 25 years for low temperature applications (T < 300 °C) [2]. In recent literature [3–5], the performance criterion (PC), based on changes in absorptance ($\Delta\alpha$) and emittance ($\Delta\varepsilon_T$) has been updated for high temperature applications (T > 400 °C) and can be described as follows:

$$PC = -\Delta\alpha + 0.5\Delta\varepsilon_T \begin{cases} PC \leq 5 & PASS \\ PC > 5 & FAIL \end{cases} \tag{1}$$

This criterion has been found to describe reasonably the ageing of the coatings in many applications [3–6] and it was evaluated that a

---

[*] Corresponding author.
E-mail address: ramon.escobar@uca.es (R. Escobar-Galindo).

https://doi.org/10.1016/j.solmat.2018.04.027
Received 20 November 2017; Received in revised form 22 March 2018; Accepted 23 April 2018
0927-0248/

maximum performance decrease of 5% could be acceptable [7]. Based in this procedure a European service life predication standard EN 12975–3-1 (2011) was developed by the European Committee for Standardization [8]. In a very recent review [3], Zhang *et al.* brilliantly summarizes the most applied thermal stability and testing methods (i.e. customized and accelerated ageing standard testing methods). The authors also described thoroughly the main ageing mechanisms, that is, diffusion and oxidation, but also microstructural and compositional changes occurring at high temperatures. They concluded that there is an urgent need of drawing up a broadly applicable test standard for the performance criterion as none of the currently applied testing methods are suitable to predict the service lifetime of solar selective coatings applied in air under high temperature conditions.

Among the potential candidates to be used as solar absorber layers in high temperature applications, Physical Vapour Deposition (PVD) deposited coatings (in particular $Al_yTi_{1-y}(O_xN_{1-x})$ based coatings) have been considered in the literature [9–14] due to their proven excellent oxidation resistance and thermal stability e.g. for high temperature machining applications [15–21]. In [14] Du *et al.* reported thermal stability in air up to 400 °C for 192 h of an $Al/Ti_{.5}Al_{.5}N/Ti_{.25}Al_{.75}N/AlN$ solar selective coating deposited on stainless steel (SS) by magnetron sputtering (MS). Barshilia *et al.* have extensively reported the characterization and high temperature performance of Ti/AlTiN/AlTiON/AlTiO SSCs deposited by MS on SS and copper substrates [10–12]. The developed coatings showed a high thermal stability during short periods (2 h) at 400 °C and after 1000 h of cyclic heating conditions (using 3 °C/minute as heating and cooling ramps) in air at 350 °C. However, both systems underwent a significant loss of their optical performance at higher temperatures. The main failure mechanisms were identified to be oxidation and diffusion. At 500 °C oxygen and nitrogen diffuse through the columnar structure of the MS deposited AlTiN layers forming Al–Ti–O–N films that destroy the optimized four-layer structure and consequently the optical selectivity of the SSC. In addition, surface colour alterations and delamination problems were observed at $T > 600$ °C for coatings deposited directly on a Cu substrate [1,12,14]. In order to prevent these failure mechanisms, and to improve oxidation resistance, thermal stability and performance in cutting tests, the incorporation of silicon into the Al-Ti-N layer structure was proposed [22,23]. Following this approach, Rebouta *et al.* [24] showed PC changes below 5% for a SSC multilayer of $TiAlSiN/TiAlSiON/SiO_2$ after 600 h of thermal treatment at 278 °C in air, while Feng *et al.* [25] reported that $TiAlSiN/TiAlSiON/Si_3N_4$ SSCs deposited on SS remained stable after heat treatments at 272 °C in air for 300 h. The combination of multilayers using different nitrides (i.e. TiAlCrN/TiAlN/AlSiN in [26]) resulted in SSCs thermally stable in air up to 400 °C for 4 h. Barshilia *et al.* recently proposed the use of a more complex stacking structure of TiAlC/TiAlCN/TiAlSiCN/TiAlSiCO/TiAlSiO [27,28], primarily due to the very high thermal stability (up to 1200 °C in air) of the individual constituent layers. Moreover, they reported that the presence of up to 6 interfaces in the system reduces the porosity and helps in blocking the formation of the typical columnar microstructure of sputtered coatings. The designed tandem absorber showed high thermal stability in air up to 500 °C for 2 h and long thermal stability up to 325 °C for 400 h. All these approaches, although valid, apply complicated and expensive processing steps jeopardizing the industrial manufacturing of the proposed SSC structures.

As alternative approach to grow thermally stable SSCs with a simpler design, we recently proposed in [29] the use of Cathodic Vacuum Arc (CVA) to promote the deposition of denser $Al_yTi_{1-y}(O_xN_{1-x})$ films with less-pronounced or even suppressed columnar morphology in order to improve the performance of the absorber coating when subjected to thermal treatments [30–32]. A set of coatings based on compositionally graded $Al_yTi_{1-y}(O_xN_{1-x})$ layers was designed and optimized with respect of their final SSC properties [29]. The goal of this second part paper is twofold: i) experimentally validate the SSC designs made in [29] and ii) assess the thermal stability of these multilayer stacks in air. In order to fulfil those objectives complete solar selective multilayers were deposited by CVA. Scanning Electron Microscopy (SEM), Elastic Recoil Detection (ERD), X-Ray diffraction (XRD), UltraViolet-Visible-Near Infrared (UV–Vis–NIR) and Fourier Transform Infrared (FTIR) spectrophotometry were applied for comprehensive compositional, structural and optical characterization. Excellent agreement was found between the nominal properties of the coatings and those of the experimentally deposited stacks, thus validating the designs based on the optical constants of each of the individual oxynitride layers. The thermal stability of these multilayer stacks in air was evaluated by i) single-stage tests of 12 h at 450, 650 and 800 °C and ii) heating–cooling cycles between 300 and 600 °C up to 900 h. Changes observed in the optical performance of the coatings upon thermal treatment were correlated with modifications of layer composition, microstructure, and morphology. The maximum working temperature of the studied multilayer coatings was 250 °C higher than the values reported for this class of materials under comparable conditions until now. Hence, the applied approach for design and development of optical coatings, based on a single-batch process technology, has led to SSCs with competitive properties for realistic operation conditions of central receiver power plants.

2. Experimental details

2.1. Thin film growth

Two SSC multilayer stacks were grown on mirror polished Inconel HAYNES ® 230 and on silicon (100) substrates at 450 °C using a commercial direct current (DC) non-filtered CVA PL70 Platit setup. Details of the deposition parameters of the individual $Al_yTi_{1-y}(O_xN_{1-x})$ absorber and antireflective layers were given in the companion paper [29]. A layer of TiN was deposited as an IR reflective film in the SSC stack employing the same experimental setup. The TiN layer was deposited at 300 °C using a 99.99% pure Ti metallic cathode and 3 sccm of N_2 gas flow. The complete SSC stack (TiN IR reflective layer/ $Al_yTi_{1-y}(O_xN_{1-x})$ absorber layer(s)/ AlTiO antireflective layer) was manufactured in a single batch process.

2.2. Thin film characterization

A Hitachi S5200 Scanning Electron Microscope equipped with a field emission gun (FEG) was employed to analyze the morphology of the deposited samples. Cross-sectional and top surface images of the samples deposited on silicon substrates were measured without metallization at 1 and 5 kV electron beam energy.

ERD analysis was used to determine the depth-resolved elemental composition of the samples. The measurements were carried out using an incident 43 MeV Cl^{7+} ion beam of a 6 MV tandem accelerator. With this experimental setup, the ERD spectra of all elements are obtained, and moreover the RBS spectrum of Ti (and possible heavy element impurities). The spectra were fitted simultaneously using the program NDF v9.3 g [33] to obtain profiles of concentration as a function of depth.

The phase structure of the SSCs was determined by X-ray diffraction employing grazing incidence geometry (GIXRD) using a Rigaku Ultima IV diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). The incident angle was 0.4°, and the XRD patterns were measured in the diffraction angle range of 20–100° in steps of 0.02°.

The reflectance at room temperature was measured under an incident angle of 11° from the normal in the 300–2500 nm wavelength range using a Perkin Elmer UV–Vis–NIR spectrophotometer Lambda 1050. A 150-mm integrated sphere accessory consisting of two hemispheres coated with Spectralon and equipped with PMT and InGaAs detectors was employed. Spectralon was used as the diffusively reflecting reference.

Mid IR reflectance was recorded in the wave number (wavelength)