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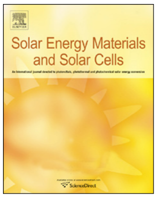

Effects of environmental and operational variability on the spectrally selective properties of W/WAlN/WAlON/Al_2O_3-based solar absorber coating

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ABSTRACT

The stability of solar selective absorber coatings in hostile environments (e.g., humid condition, corrosive medium, longer exposure at elevated temperature) needs to be critically assessed to ensure durability of such coatings. In the present work, magnetron sputtered W/WAlN/WAlON/Al_2O_3-based absorber coating with a high absorptance (0.958) and low emittance (82 °C) has been tested in humid and corrosive environments. The selectivity (absorptance/emittance) of the coating did not change after keeping it in 95% humidity at 37 °C for 400 h. Corrosion study in 3.5% NaCl solution reveals that this novel multilayer coating has a better corrosion resistance than that of uncoated stainless steel (SS) substrate. The nanoindentation test on the coating indicates that it has a hardness of 9.6 ± 0.5 GPa. The performance of the coating did not degrade after heat treatment at 350 °C in air for 1000 h. Additionally, the activation energy for degradation has been determined to predict the stability of the coating at high temperature. Further, the normal spectral emissivity of the tandem solar absorber was measured in the full angular range from 200 to 500 °C. The results of emissivity measurements by varying observation angles are analysed using numerical integration to obtain the total hemispherical emissivity. In summary, W/WAlN/WAlON/Al_2O_3 stack is an attractive candidate absorber coating for photo-thermal conversion systems.

1. Introduction

A spectrally selective solar absorber coating should possess a very high absorptance ($\alpha \geq 0.95$) in the solar spectrum (0.3–2.5 μm) and a low emittance ($\varepsilon \leq 0.05$) in the infrared region (2.5–25 μm) for an efficient photothermal conversion [1]. Along with the superior combination of absorptance and emittance, the absorber should also perform at high temperature. Exceptional resistivity against thermal stresses, low thermal expansion coefficient, long thermal durability, thermo-chemical and thermo-mechanical stability are some of the critical parameters for solar selective absorber coatings [2]. These necessary properties can be ensured by a multilayer structure where the metallic properties decrease from substrate to surface. During last few years, multilayer architectures, including TiAlSiN/TiAlSiON/SiO_2 [3], $Ti_{0.5}Al_{0.5}N/Ti_{0.25}Al_{0.75}N$/AlN [4], RuO_2/SiO_2 [5], HfMoN/HfON/Al_2O_3 [6], etc. have been studied extensively.

Long term durability of the absorber coatings can be determined by investigating their behaviour in harsh environment as the functionality of the solar absorber coating can be affected by various environmental issues. Therefore, several experiments on these coatings are extremely needed to assess their performance in adverse conditions. There are a few studies on the selective coatings concerning their mechanical stability, corrosion resistance, performance in humid environment, scratch resistance, etc. For example, Gao et al. [7] demonstrated anti-corrosion property of TiC/Al_2O_3-based solar absorber. Ti/AlTiN/AlTiON/AlTiO-based spectrally selective coating, developed by Barshilia [2], exhibited a superior combination of high spectral selectivity, improved adhesion, UV stability, corrosion resistance and high thermal stability. Amri et al. [8] evaluated elastic modulus and hardness of cobalt-based metal oxide ($M_xCo_yO_z$ with M = Mn, Cu, Ni) thin solar absorber films and observed that such coatings exhibit appreciable mechanical stability.

Along with physical and mechanical stability, the emittance of the spectrally selective coating at elevated temperature is extremely important as high temperature emittance determines the rate of heat loss from the selective absorber surface. The infrared emittance is the metric to evaluate how well a surface radiates thermal energy in the infrared

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wavelength range as compared to a perfect black body operating at the same temperature. The total hemispherical emissivity (ε) is represented as,

$$\varepsilon = \frac{W}{W'} \tag{1}$$

where W and W' are the radiant emission from a real and perfect black body, respectively [9]. The emittance of a body can also be determined using Plank's radiation law,

$$N_\lambda = \frac{\varepsilon_\lambda C_1}{\lambda^5[\exp(C_2/\lambda T)-1]} \tag{2}$$

where λ is the wavelength, T is the absolute temperature, and C_1 and C_2 are the Planck constants.

Emissivity of a material is dependent on temperature, wavelength and surface condition. It can have a value between 0 (perfect reflector - mirror) and 1 (perfect emitter - black body). The total hemispherical emissivity at a particular wavelength can be obtained by

$$\varepsilon_H(T) = \frac{1}{\pi}\int_0^{\pi/2}\int_0^{2\pi} \varepsilon_T(\theta, T)\cos\theta\sin\theta d\theta d\varnothing \tag{3}$$

where $\varepsilon_T(\theta, T)$ is the total directional emissivity and $\varepsilon_H(T)$ is the total hemispherical emissivity at temperature T [10].

The photothermal application of the absorber demands a very low emittance, i.e., less amount of heat loss at high temperature as thermal radiation from a surface increases proportionally by T^4. Recently, a little research attention has been devoted to acquire overall understanding of the radiative properties of these coatings. For example, Setién-Fernández et al. [11] first introduced a radiometric characterization of Mo-SiO_2-based double cermet coating at the entire working temperature range (150–600 °C). The emissivity study by Echániz et al. [12] on Mo–Si_3N_4-based spectrally selective coating from 250 to 600 °C for a number of heating cycles proved good performance for high temperature photo-thermal applications. In a separate study, the high temperature emissive properties of TiAlC/TiAlCN/TiAlSiCN/TiAlSiCO/TiAlSiO-based multilayer absorber coating was determined by Jyothi et al. [13]. It was found that the coating exhibited promising selective properties up to 500 °C. Therefore, it can be interpreted that in order to evaluate the performance of solar selective coating in actual field, a complete knowledge on environmental stability and high temperature emissivity is essential.

In our previous work, we designed a coating of W/WAlN/WAlON/Al_2O_3 with graded metallic structure, which showed an excellent selectivity with a high absorptance of 0.958 and low emittance of 0.08. The thickness of the individual layer of W, WAlN, WAlON and Al_2O_3 was found to be ~ 125, 40, 40 and 62 nm, respectively. The layers were clearly distinguishable in terms of compositional variation [14,15]. We also investigated long term thermal stability of the coating and found that the coating was thermally stable at 350 and 500 °C for 550 and 150 h, respectively in air [16,17]. In the present study, the optical properties of the coating have been examined in humid environment. In order to support self-cleaning property of the coating, the contact angle of the coating with water has also been measured. The corrosion studies have been performed on bare and coated stainless steel substrates using electrochemical technique. The coating/substrate adhesion has been investigated by scratch test. Nanoindentation test has been carried out to obtain an idea about hardness of prepared thin film. Most importantly, we report here the long term thermal stability of the W/WAlN/WAlON/Al_2O_3 coating at 350 °C in air for 1000 h. The emissive properties of the coating have been explored from 200 to 500 °C. In order to understand the underlying optical phenomena of the coating in the entire spectrum, we have investigated the dependence of emissivity with angle of observation and have evaluated the total hemispherical emissivity of the coating.

2. Experimental

The W/WAlN/WAlON/Al_2O_3-based solar selective coating, shown in Fig. 1, has been deposited on stainless steel (SS) substrates by DC and RF magnetron sputtering using highly pure (> 99.9%) W, Al and Al_2O_3 targets. The SS substrates were mechanically polished using emery papers, followed by diamond nanoparticle suspension. The deposition chamber was evacuated to a base pressure of 8.0×10^{-4} Pa by means of rotary and turbomolecular pumps. W, WAlN, WAlON and Al_2O_3 layers were deposited successively in Ar, Ar + N_2, Ar + N_2 + O_2 and Ar + O_2 environments. The depositions were carried out at a substrate temperature of 300 °C. A number of parameters, such as target power, reactive gas flow, and deposition time were tailored to achieve a maximum solar absorptance and low thermal emittance. The details of the deposition method can be found elsewhere [14].

To carry out the humidity test, the samples were placed at nearly 95% humidity at 37 °C for 400 h. The reflectance spectra of the coating were collected before and after humidity test. The surface wettability of the coating was studied by measuring contact angles using sessile drop method with distilled water. The inspection was performed by contact angle goniometer (Dataphysics OCA 15EC) and a microscope that combine together charge-coupled device (CCD) camera and digital imaging techniques under ambient condition. A dosing volume of 5 µL was dispensed on the coating with a speed of 0.10 µL/s. The contact angle of the samples was measured at three places and the value reported herein is the average of three measurements.

The corrosion behaviour of substrate and coating was performed using a three-electrode electrochemical cell set-up in a 3.5% sodium chloride solution under free air condition at room temperature. In the electrochemical cell, a platinum plate of 1 cm^2 area and an Ag/AgCl, 3 M KCl electrode were fixed as counter and reference electrodes, respectively. The experimental procedure has been demonstrated in detail elsewhere [18].

Scratch adhesion test was performed using nano scratch tester (Bruker's Scratch Test System, USA). The coating was scratched by a Rockwell diamond indenter with the tip radius of 200 µm with a linearly increasing normal load from 1 to 4.5 N for 1 mm distance at a speed of 0.02 mm/s. The hardness of the absorber coating was estimated using nanoindenter (Hysitron Triboindenter, Minneapolis, MN, USA), equipped with a three-sided pyramidal Berkovich diamond indenter. The equipment records the load (*P*) and penetration depth (*h*) of the indenter with resolutions of 1 nN and 0.2 nm, respectively. A peak load (P_{max}) of 1000 µN with loading and unloading rate of 200 µN/s was used. The recorded data were analysed using the standard Oliver-Pharr method [19] to obtain the hardness (H) of the multilayer film.

The absorptance and emittance of the selective absorber were measured using solar spectrum reflectometer and emissometer (M/S Devices and Services). An UV–Vis–NIR spectrophotometer (PerkinElmer, Lambda 950), equipped with an integrating sphere was utilized to evaluate the reflectance spectra of the coating at the incidence angle of 0°. In order to evaluate thermal stability, the coating was subjected to 350 °C for 1000 h inside a tube furnace (Carbolite).

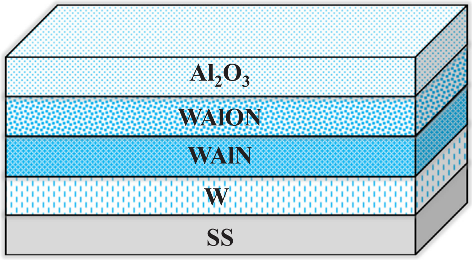

Fig. 1. Schematic representation of W/WAlN/WAlON/Al_2O_3-based absorber coating on SS substrate deposited by magnetron sputtering.