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Thermal stability of $WAlN/WAlON/Al_2O_3$-based solar selective absorber coating

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Abstract

The solar absorptance property of $W/WAlN/WAlON/Al_2O_3$-based coatings, deposited by DC/RF magnetron sputtering on stainless steel substrate was studied by measuring the reflectance spectra in the wavelength range of 250 - 2500 nm. The effect of thermal annealing on the optical properties of the solar selective absorber coatings was investigated. Annealing the coatings at 450°C for 150 hrs in air did not show any significant change in the spectral properties of the absorber coating indicating the excellent thermal stability of the coating. The W layer acts as infrared reflective layer and diffusion barrier on stainless steel substrate. The top Al_2O_3 layer serves as dense shield to protect the under layers from oxidation in air. In summary, the present study indicates the potential application of $W/WAlN/WAlON/Al_2O_3$-based selective coatings in high temperature photo thermal conversion systems.

Introduction

Solar energy is one of the reliable sources of energy to meet the ever-increasing demand of renewable energy. In this regard, concentrating solar power (CSP) is the emerging system for photo-thermal conversion of solar energy. Solar energy can be converted to thermal energy and subsequently the thermal energy can be used to generate electricity in CSP systems [1]. There are numerous components of the CSP systems like, several mirror configurations, receiver tube, heat transfer fluid, thermal energy storage etc [2]. Among all the components, the performance of the CSP systems depends on the receiver tube. The efficiency of a CSP system can be increased if the solar energy absorbed by absorber coating on the receiver is maximized while the heat loss from the receiver to the environment is minimized. The highest photo thermal conversion efficiency is to be expected when the coating is able to absorb most of the solar radiation spectrum (0.3–2.5 μm), giving the coating a high solar absorptance ($\alpha > 0.90$) whereas the heat losses in the infrared region (2.5 – 25 μm) is very less (< 0.10). To be a potential candidate as an absorber coating in CSP systems, along with high α and low ε, the coating should have thermal stability up to very high temperature [3]. The coatings which sustain in the temperature more than 400°C are known as high temperature solar selective absorber coating. In last few decades, intense efforts have been given by many researchers for searching thermo-stable solar selective coating as there is no intrinsic material to exhibit solar selectivity and thermal stability at the same time. Therefore, there is a serious demand of stacking different materials to form a multilayer coating for achieving the desire selectivity as well as thermal stability [4]. Among different kind of selective coatings, a special attention has been given to graded tandem absorber due to it's exceptionally good selective property and thermal stability. The metal volume fraction of the graded tandem absorber decreases from substrate to surface. The typical coating consists of an infrared reflective metallic layer, a high metal volume fraction solar absorption layer, a low metal volume fraction semi-absorber layer and a transparent anti-reflection layer [5].

In recent years, graded metal oxides and oxinitride coatings developed by sputtering techniques have been intensively studied. These coatings exhibited outstanding performance due to their attractive optical properties, chemical inertness, high melting point and thermal stability. A large number of transition metal nitride and oxintrides solar selective coatings, such as TiZrN/TiZrON/SiON, AlSiN/AlSiON/$AlSiO_y$, TiAlN/TiAlON/SiO_2 etc have been investigated[6-8].

In our recent work, we developed W/WAlN/WAlON/Al_2O_3- based solar selective coating on stainless steel substrate by reactive DC and RF magnetron sputtering. The coating showed excellent selectivity with an absorptance of 0.958 and emittance of 0.08. Along with that we studied the short term thermal stability of the coating by annealing the coating from 300 – 550 °C for 2 hrs in air [9]. In the present work, we have investigated the optical properties of W/WAlN/WAlON/Al_2O_3 –based multilayer solar selective absorber coating if exposed at high temperature (450°C) in ambient air atmosphere for long time (150 hrs).

Experimental:

At the first stage, the stainless steel substrates were mechanically polished. The typical size of the substrates were 3.5 X 3.5 X 2 cm. These dimensions were suitable to measure the hemispherical absorptance and thermal emittance of the coating. After polishing the substrates were cleaned by deionized water, ethanol and acetone. The tandem absorber was deposited on stainless steel substrates by DC and RF magnetron sputtering under a base pressure of 8.5×10^{-6} mbar. The multilayer stack was made of W, WAlN, WAlON and Al_2O_3 layers by using W, Al and Al_2O_3 targets with 99.99% purity. The W layer was deposited in Ar atmosphere. WAlN was prepared with a variation of N_2 gas flow in Ar + N_2 environment whereas for WAlON film, a reactive gas mixture of Ar + O_2 + N_2 was used. The deposition of Al_2O_3 was also performed in Ar + O_2 environment to ensure the presence of sufficient oxygen. The deposition parameters of the coating can be found elsewhere [9]. The design of the coating has been presented in Fig 1.

Similar kind of coating structure, made of NbAlN/NbAlON/Si_3O_4 was fabricated from our group in a base pressure of 5×10^{-4} Pa. The XPS study of the coating indicates the formation of NbAlN layer without any trace of oxygen [10]. Therefore we have kept similar base pressure to find out the feasibility in fabricating WAlN layer.

Our recent work demonstrates the structural and composition characterization of WAlN, WAlON and Al_2O_3 layers [9]. Each layer was deposited individually on stainless steel and Si substrates for longer duration keeping other deposition parameter constant. The phase assemblage of the film was investigated by X-Ray Diffractometer (Bruker, D8) with Cu-K_α (40 kV, 40 mA, $\lambda = 0.15406$ nm) radiation in the 2θ range of 10° to 60°. Formation of nano-crystalline WN and WO_3 has been found in WAlN and WAlON layer, respectively while the Al_2O_3 layer was amorphous in nature.
The chemical composition and bonding structure of the coatings, deposited on Si substrates were probed by X-ray photoelectron spectroscopy (SPECS), using non-monochromatic Al K_α radiation (1486.8 eV). The XPS spectra of individual layer for W 4f, Al 2p, N 1s and O 1s have been analysed. The XPS study of present WAlN/WAlON/Al_2O_3 also indicates the formation of WAlN layer. A peak of WO_3 has been found in the WAlN layer. The formation of WO_3 can be attributed to the presence of small amount of residual oxygen inside the chamber.

The long term thermal stability of the coating was not investigated in the recent work. In the present work, we have studied the effect on the heat treatment on the optical properties of the coatings after heat treatment at 450 °C in air for 150 hrs.

The optical properties of the coatings were measured by an UV-VIS-NIR spectrophotometer (PerkinElmer, Lambda 950) in the wavelength range of 250 – 2500 nm at near normal incident angle. The instrument is equipped with an integrating sphere for measurements of diffuse reflectance of the coating. The absorptance and emittance of the coatings were measured by solar spectrum reflectometer and emissometer (M/s. Devices and Services). The absorptance was measured at near normal incidence. The accuracies of the measured absorptance values are ±2% with a drift of ±1% +0.003/h while the emissometer has a repeatability of ±0.01 units. The absorptance and the emittance values were measured at four different positions of the samples, and the values reported herein are the average of four measurements.

Al_2O_3 (Dielectric)
WAlON (Metal-dielectric composite)
WAlN (Metal-dielectric composite)
W (IR reflector)
Stainless steel (Substrate)

Fig. 1. Schematic of W/WAlN/WAlON/Al_2O_3-based absorber coating

Results and discussions

High solar absorptance and thermal emittance are the two important parameters to evaluate the performance of a solar selective coating. When electromagnetic wave interacts with a surface, some fraction of the electromagnetic wave is reflected back by the surface, some portion is absorbed inside the material and the rest of the portion is transmitted. According to conservation of energy, the total energy of the incident wave is sum of the energy of the reflected, absorbed and transmitted waves. Therefore, the interaction of the EM wave with the surface can be written by the following equation [11].

$$R(\lambda) + \alpha(\lambda) + T(\lambda) = 1 \qquad \text{---- (1)}$$

Where R(λ), $\alpha(\lambda)$ and T(λ) represent the reflectance, absorptance and transmittance at wavelength λ, respectively. For the collector tube, the selective absorbers usually be coated on stainless steel tube. Considering negligible transmittance i.e. T(λ) = 0 for stainless steel, R(λ) and α(λ) can be related as shown in Eq. 2:

$$\alpha(\lambda) = 1 - R(\lambda) \qquad \text{---- (2)}$$

The absorptance value can thus be estimated from the diffuse reflectance data using the eq. 2. According to Kirchhoff's law, at thermal equilibrium, the value of absorptance α(λ) at a particular wavelength is equal to the value of emittance, ε(λ). The thermal emittance of the coating increases with fourth power of temperature [12]. Therefore, it is very relevant to study the effect of temperature on the optical properties of the coating.

Table 1 represents the absorptance and emittance value of as-deposited and annealed coatings. The absorptance and emittance of the as-deposited coating was 0.958 and 0.08. After heat-treatment at 450 °C for 150 hrs decreased to 0.920 and emittance increases to 0.11. The insignificant change in the absorptance ($\Delta\alpha$ = 0.038) and emittance ($\Delta\varepsilon$ = 0.03) values can be attributed to high thermal stability of the coating. For further confirmation, the reflective behaviour of as-deposited coating and annealed coating for 80 hrs, 100 hrs and 150 hrs at 450 °C in air were investigated.

Table 1: Absorptance and emittance of as-deposited and heat-treated coatings

Coating	Absorptance	Emittance
As-deposited	0.958	0.08
Heat-treated	0.920	0.11

To absorb maximum absorptance in the solar spectrum, the metallic property and the refractive index of the coating should decrease from substrate to surface of the coating. Therefore, a gradual change in the refractive index and the metallic property has been introduced in WAlN/WAlON/Al_2O_3 coating so that the double interference absorption theory can be satisfied to enhance the solar absorptance[13]. The desired architecture of coating has been achieved by tailoring the target power, deposition time and O_2/N_2 gas flow rates. The common absorption phenomenon by destructive interference has been observed in the as-deposited as well as the heat treated coatings[14]. The interference maxima around 450 nm in the reflectance spectra of all the coatings clearly indicates that the main contribution in absorption has come from destructive interference. A sharp interference minimum has been observed at 356 nm. The high absorptance of the coating is also evident from another wide interference minimum covering wavelength of 870 to 1345 nm. The reflectance in the wide minimum is ~ 0% which leads to the maximum absorptance in the coating. Meanwhile, obvious higher reflectance has been observed from 1500 nm which reaches to ~ 50% at 2230 nm, leading to relatively lower emittance.

A slight increase in the reflectance has been observed in the reflectance spectra of all the heat treated coatings (see Fig. 2a). The shift of the interference maximum towards shorter wavelengths has also been observed in the coating after annealing at 450 °C for 80, 100 and 150 hrs in Fig. 2b. The sudden exposure of the coating at elevated temperature leads to the preliminary change in the reflectance spectra. However, the negligible change in the reflectance does not affect the optical performance of the coating which has already been confirmed from the absorptance and emittance value of the as-deposited and heat treated coatings.

The slight increase in the reflectance in the heat treated sample for 80 hrs has been observed due to sudden exposure of as-deposited coating into elevated temperature. After that, the reflectance did not change significantly for 100 and 150 hrs. The increase in the reflectance has been observed in the interference maxima of heat treated coatings. However for longer wavelength the change in the reflectance is insignificant. The reason of the increase in the reflectance maxima can also be explained by interference mechanism. The thickness of the coating might have changed due to the heat treatment for such a longer time. The destructive interference which is dependent on the thickness of the layers, has been affected. Therefore, less amount of incident light has been trapped in the absorbers layer, resulting an increase of reflectance in the interference maxima. No interference minima or maxima has been observed in the longer wavelength of the reflectance spectra of the coating. Therefore it can be concluded that the destructive interference does not play an important role for the absorption in the longer wavelength. Hence, the change in the reflectance spectra has not been observed.

The emittance may increase due to several factors like compositional change, increase in surface roughness and the reaction between individual layers at elevated temperature. In the present case, the emittance is sensitive to the oxidation of W layer also. The infrared radiation is reflected by the W layer and the oxidation of the layer might have changed the reflectance properties and thus the emissivity. However all this changes are irreversible even if sample comes back to room temperature. As the emittance has not increased after heat treatment for such a long time, it has been concluded that no such processes occurred during heat treatment.

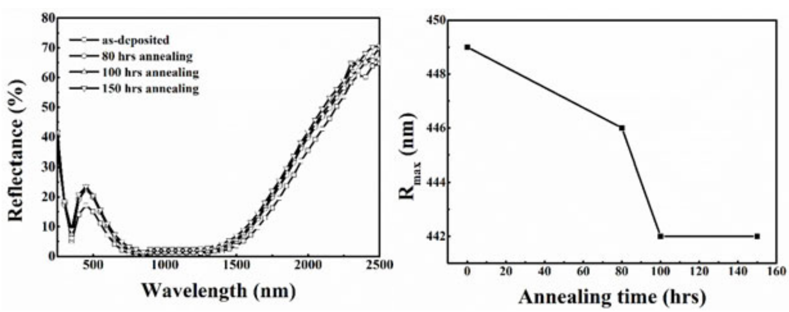

Fig 2: (a) The reflectance spectra of as-deposited and heat-treated coating at 450 °C in air for 80, 100 and 150 hrs; (b) The dependence of annealing time and reflectance maxima

Peeling effects in the coating have not been observed which indicates good adhesion of the individual layers to the substrate and to each other is achieved. The high thermal stability of the coating can be attributed to various reasons.

High temperature heat-treatment could induce microstructure degradation such as inter-diffusion and reaction at the interface resulting in phase decomposition, transformation, and oxidation, as investigated in other works. The optical properties are very sensitive to any changes in the coating composition and the reflectance spectra of the as-depsoited and heat treated coating as well as the absorptance and emittance valued show that those processes do not take place during heat treatment. The high temperature stability of the coaring depends on various factors. In the present work, W layer serves as diffusion barrier and restricts the reaction between stainless steel substrate and absorber layer. As a result, no complex phases formed which could be responsible for reducing the efficiency of the absorber coating. The WAlN layer composed of AlN and WN phases is believed to be good diffusion barrier, indicating a minimal dissusion between the layers. The WAlON consists of AlON which has very high oxidation resistance (1000 °C), stable microstructure, and high activation energy [8]. The anti-reflection layer of Al_2O_3 together with WAlON, respectively retard the oxygen penetration from air to prevent main absorber WAlN layer and W oxidation.

Conclusions

W/WAlN/WAlON/Al_2O_3 –based coating, deposited on SS substrate by reactive DC and RF sputtering, exhibited high absorptance of 0.958 and a low emittance of 0.08. The solar selective proeprties of the coating underwent insignificant changes after heat treatment for 150 hrs at 450 °C in air. The absorptance and emittance of the coating changes to 0.920 and 0.11, respectively after annealing. Reflectance spectra of as-deposited and heat treated coating also indicate the excellent selective property of the coating even after heat treatment. In summary, W/WAlN/WAlON/Al_2O_3 is a very promising coating for high temperature CSP systems.

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