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Optimization procedure and fabrication of highly efficient and thermally stable solar coating for receiver operating at high temperature

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ABSTRACT

In "parabolic trough" technology for concentrating solar plants, optimization and fabrication of effective and thermally stable solar coatings represent the most challenging technological goal in order to maximize the photo-thermal conversion efficiency of a solar field operating at high temperature. Starting from the typical cermet-based thin film stratification constituting high-performance solar coating, the optical properties of the metallic layer deposited as "back reflector" strongly determines the thermal loss amount, where solar coating emissivity should have to be as low as possible. Thanks to its very high reflectance in the infrared region, silver is more promising respect to transition metals such as molybdenum and tungsten. An adaptive tungsten layer deposited on stainless steel substrate has been employed with the aim of promoting improvements both on adhesion and on thermal stability of the Ag infrared reflector. Optimization procedure has been in detail described to design and to realize effective cermet-based solar coatings. Six different solar coatings with Ag as back reflector have been optically designed by means of a semi-empirical procedure where a layer-on-layer ellipsometric characterization was utilized. These optimized coatings were fabricated at increasing solar absorptance values coupled with emissivity values, evaluated at 580 °C, lower than 14%. Improved performances have been obtained respect to similar optimized solar coatings with W as back reflector and the highest photo-thermal conversion efficiency has been reached (> 92% at 400 °C and > 85% at 550 °C) among the solar coatings at the present state of the art. Excellent thermal and optical stability has been proved by means of annealing cycles at 580 °C under vacuum for a total duration of 85 days.

1. Introduction

Spectrally selective coatings used in solar evacuated receiver tubes, employed in concentrating solar plants (CSP) with "parabolic trough" technology, are known to improve the photo-thermal efficiency in terms of high solar radiation absorptance (α_s) and low thermal emittance (ε) at the operating temperature [1]. This aim can be achieved using a multilayer structure: a metallic layer with high reflectivity in the infrared region to assure a low emittance value, a cermet layer to absorb incoming solar radiation and an anti-reflection layer to minimize reflection losses. Cermet is a particular composite material formed by bonded particles of ceramic and metal.

Since 2001, the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) has been involved in projects for the development of concentrating solar plants for high temperature heat generation with the "parabolic trough" technology. These plants employ molten salts as thermal exchange fluid, entering at 290 °C in the solar field and coming out at 550 °C. As a consequence, the coating temperature will be about 300 °C at the beginning of the solar field and about 580 °C at the end. At ENEA laboratories, solar coatings for high temperature applications were designed and fabricated with molybdenum and tungsten as metallic layer [2,3]. These solar coatings showed good photo-thermal performance and high thermal stability up to the operating temperature of 580 °C under vacuum (10^{-2} Pa inside the interspace of the encapsulating glass). During the last years, big efforts have been performed by ENEA researchers and, more generally, by the scientific community to enhance the photo-thermal performance of solar coatings for high temperature applications, being this technological goal of great impact on the overall efficiency of solar thermodynamic plants and on the future prospects of success for the entire solar thermal power technology.

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A way to increase the photo-thermal performance of solar coatings consists in employing metals stable at high temperature with optical reflectance very close to 100% in the infrared region, because high reflectance enables to fabricate solar coatings with the lowest thermal emittance for a given solar absorptance. Although tungsten and molybdenum exhibit high thermal stability up to 580 °C [2–5], their reflectance in NIR–IR spectral region is not enough high if compared with that of noble metals such as silver [6]. Silver is a very attractive material for applications in solar coating technology because it has the highest infrared reflectance over an extended wavelength range [6] and its higher cost is compensated by the back reflector thickness that is significantly smaller than W and Mo back reflector thicknesses to obtain the same infrared reflectivity [7].

Furthermore, it is important to emphasize the different optical behavior of Ag respect to W at the increase of temperature: as will be shown in the next sections, the infrared reflectance decrease at 580 °C is very small for the heated noble metal and is rather large for the heated transition metal. As a consequence, the good performance in terms of low emissivity at increasing temperature is better assured by using Ag as metallic layer. However, the use of Ag presents two main limitations. First of all, Ag thin films deposited on oxidized surfaces, such as stainless steel (SS) surfaces of evacuated receiver tubes, show poor adhesion due to non-uniform substrate coverage and detrimental morphological modifications, such as dewetting and coalescence phenomena [8], when it is subjected to thermal cycles. Furthermore, Ag has a large diffusion coefficient at elevated temperature [9–11] and atomic diffusion into the adjacent layer could occur with degradation of photo-thermal performance of the solar coating. In order to prevent this phenomenon, an approach employed with success in the solar coating technology consists in the Ag layer packing between barrier layers [7]. Recent studies carried out at ENEA laboratories [12] have shown that an alternative solution to this problem is the deposition of an adaptive layer of W deposited on SS substrate that is able to promote improvements both on the adhesion and on the structural stability of Ag infrared reflector. Moreover, annealing processes performed under vacuum (10^{-2} Pa) at 400 °C for 29 days on a cermet-based selective coating with Ag as infrared reflector and W as adaptive layer showed an excellent thermal and optical stability of the multilayer structure.

Starting from these results, the successive step, topic of this article, was the design and fabrication of solar coatings with Ag as infrared mirror, optically and structurally stable up to the operating temperature of 580 °C. These coatings consisted of a tungsten nitride-aluminum nitride (WN-AlN) graded cermet layer (absorbing layer) deposited between Ag/W double layer (back reflector) and an antireflection filter, composed of materials with high transparence and appropriate refraction index such as silica (SiO_2), aluminum nitride (AlN) and WN-AlN cermets with very low metal volume fraction. The refraction index (n) and the extinction coefficient (k) of all materials, which could potentially form the spectrally selective coating, were estimated by ellipsometric technique and organized in a database. Therefore, six solar coatings were optically designed with increasing solar absorptance values by using two software tools. The former was a homemade software for optical design of multilayer structures with graded cermet as absorbing layer, the latter was Macleod, a commercial software for the optical analysis of multilayer structures, suitable to refine the output of the first tool. The “receipts” of all the six optical designs were employed to fabricate solar coatings by sputtering technique and each coating was optically characterized in order to obtain photo-thermal performance estimation in the range of temperature 300–580 °C. Finally, the coating with the best photo-thermal performance in the range 300–580 °C was chosen for thermal stability analysis. This coating was subjected to 7 cycles of annealing at 580 °C under vacuum for a total amount of 85 days and, at the end of each cycle, the photo-thermal performance was estimated to evaluate the thermal and optical stability of the coating. Pull tests were also performed both on the “as grown” coating and on the coating at the end of the heat treatments to assess the adhesion strength of the coating on SS substrates.

2. Experimental section

Metallic, ceramic and cermet films of the spectrally selective solar absorbers were deposited by sputtering technique using a proprietary planar magnetron sputtering system equipped with process chamber and load lock chamber. In the process chamber six cathodes are mounted, arranged in pairs on two opposite sides, specifically, three Standard Magnetron and three Dual Magnetron cathodes. The Standard Magnetron cathodes can be operated in DC and DC Pulsed sputtering mode, whereas the Dual Magnetron cathodes can be operated in Bipolar DC pulsed and MF sputtering mode. In the load lock chamber, plasma etching and heating pre-treatments can be performed on substrates.

Each multilayer structure and single film of this experiment was deposited on glass and SS planar substrates fixed inside housings on the external surface of a SS tube (L = 60 cm, D = 7 cm). This tube-holder moves back and forth with respect to the targets with adjustable sweep velocity and, at the same time, rotates with adjustable spin velocity.

W adaptive layer and Ag infrared reflector were deposited in sequence on SS substrates pre-treated by ion plasma etching. The process carried out to pre-treat was performed in an argon plasma environment at a pressure of 1.5 Pa and by applying 3 kV DC voltage to the tube-holder. After pre-treatment, the tube-holder was moved in the process chamber to deposit multilayer structures. The ultimate pressure before starting with deposition processes was $8 \cdot 10^{-5}$ Pa and each deposition was performed after 3 min pre-sputtering process. Ag infrared reflector was grown in DC sputtering mode at Ar pressure of 1 Pa and with 4.39 W/cm^2 power density applied to the cathode. The spin velocity of the tube-holder was 30 rpm and the carrier sweep velocity was 200 cm/min. W adaptive layer was deposited in DC sputtering mode at Ar pressure of 0.4 Pa and with 6.71 W/cm^2 power density applied to the cathode. The spin velocity of the tube-holder was 15 rpm and the carrier sweep velocity was 50 cm/min.

Six WN-AlN cermet samples were deposited by reactive sputtering under an atmosphere containing nitrogen and argon, moving and rotating the tube-holder back and forth respect to Al target and W target arranged in two opposite sides (co-sputtering mode). The pressure of the Ar–N_2 mixture in the process chamber was 1 Pa and this condition was obtained with Ar flow of 200 sccm and N_2 flow of 70 sccm. These flow values enabled to operate with the Al target in reactive mode [13,14] for any power density applied to the W target and, therefore, to deposit a highly transparent ceramic component. The six samples were deposited applying a constant power density of 5.17 W/cm^2 to the Al target whereas the cathode power densities applied to the W target are reported in Table 1. Furthermore, the sweep and spin velocities were 300 cm/min and 60 rpm, respectively. The high sweep velocity enabled to deposit very thin layers due to very low resident time of the substrate in front of the two targets and, at the same time, the high spin velocity produced cermet materials with high transparence in the NIR-IR spectral region because the metallic particles dispersed in the ceramic matrix had very small dimensions. This feature of the cermet materials was very useful in the fabrication of solar coating because it allowed to minimize the optical absorption of cermet layers in the NIR-IR region and,