

Influence of Using Different SiO₂ Antireflective Coatings and Sintering Conditions on the Durability and Optical Performance of the Selective Solar Absorber

Meryem Farchado¹, Gema S. Vicente¹, Nuria Germán¹ and Ángel Morales¹

¹ CIEMAT-Plataforma Solar de Almería, Madrid (Spain)

Abstract

A multilayered absorber for low temperature thermal applications on aluminum substrate (Al-CuMnO_x/FeMnCuO_x/SiO₂) has been reported in the previous work. It is based on a single layer of CuMnO_x as absorber material and two antireflective (AR) coatings deposited by the dip-coating method. Given the appealing values of solar absorptance (0.957) and thermal emittance at 100°C (0.038) reached for this three layers configuration, an additional research was carried out for completing the feasibility study of the proposed absorber. As this selective absorber is intended to use in low-temperature solar collectors which operate in outdoor conditions, it has to accomplish the crucial requirement to withstand some ambient conditions such as high humidity and high temperatures, among others. Therefore, with a view to achieve the best durability performance of the selective absorber, a comparative study focused on using two different SiO₂ antireflective solutions as third layer and different sintering conditions of this specific layer was carried out. The influence of this layer on the optical parameters as well as the long term durability of the final selective absorber has been studied.

Keywords: Selective absorber, spinel, antireflective coating, dip-coating, optical properties, durability tests.

1. Introduction

Nowadays, renewable clean energy plays an important role in the attempt of minimizing the environmental pollution and ecological destruction as consequence of the large amount of fossil energy consumption in the world. One of the preventive measures already taken is based on promoting the use of the pollution-free solar energy. Taking advantage of the solar radiation, several applications can be covered such as space heating, domestic hot water, industrial process heating, desalinated seawater or generation of solar electricity.

Many efforts have been put in the development of different technologies for solar thermal collectors (STC); acquiring special interest the durability studies of the selective absorber coatings during the last two decades (Colangelo et al., 2016; Diamantino et al., 2016, 2017). As it is well known, the absorber is the key component of the thermal system, playing his performance an important role in solar-thermal conversion efficiency (Yang et al., 2016). Concretely, high conversion efficiencies are obtained by using solar selective absorbers whose surface implies a minimum reflection in the solar spectrum region and the maximum reflectance in the infrared wavelength region (Joly et al., 2014). Besides, to be categorized as commercially competitive, these selective absorbers should absorb at least 95% of the incoming radiation and should have a thermal emittance lower than 0.05 (Amri et al., 2014). However, manifold outdoor conditions can significantly deteriorate the material's performance. Therefore, in order to ensure a successful solar selective absorber, selective coatings have to possess long-term performance stability apart from achieving good spectral selectivity.

Some papers have found the degradation processes that can undergo the solar absorbers as consequence of high temperature, high humidity, water condensation, and airborne pollutants (Kotilainen et al., 2015; Brunold et al., 2000). In the specific case of selective absorbers, the degradation reactions and layers modifications are mainly caused by high temperatures, high humidity and condensed water (Dudita et al., 2015). Concretely, high temperatures can speed up oxidation processes and high levels of humidity may create hydrolytic reactions i.e.

electrochemical corrosion (Boström et al., 2005; Chen and Boström, 2016). All these processes can lead to variations in the optical properties. Taking into account these devastating consequences, the aim of this work is to determine the best stable antireflective material (SiO₂ antireflective coating) for the proposed Al-CuMnO_x/FeMnCuO_x/SiO₂ absorber, focusing mainly on its ability to withstand successfully the accelerated ageing tests.

2. Experimental

Prior to the dip-coating deposition of the constituent absorber films, a chemical etching treatment (10 seconds in a 5% HF solution) of the aluminum substrate was performed in order to guarantee homogeneous layers. Afterwards, the layers deposition was carried out at the optimized withdrawal rates of 42 cm/min for the CuMnO_x film, 18 cm/min for the first FeMnCuO_x antireflective coating and 12 cm/min for the SiO₂ antireflective coating (Farchado et al., 2018).

The CuMnO_x and FeMnCuO_x solutions were prepared from the metallic precursors of Cu(NO₃)₂ (Sigma Aldrich, 98-103%), Mn(NO₃)₂ (Panreac, 97%) and Fe(NO₃)₃ (PRS Panreac, 98%) at molar ratios of 1:1 for CuMnO_x and 1:1:2 for FeMnCuO_x and the absolute ethanol as solvent. A complexing agent and a wetting additive were also added to stabilize the solution and improve the film adherence (Morales, 2002). In relation to the SiO₂ antireflective layer, two kinds of silica were tested: A1 based on the high-density silica prepared using a two-step methodology under reflux conditions at 60°C (Morales and Durán, 1997) and A2 referred to the silica solution prepared without any reflux system and at room temperature. Both SiO₂ solutions were prepared maintaining unchanged their composition but varying their preparation methodology. Both solutions were obtained by dissolving the Tetraethyl ortosilicate (TEOS) precursor in a solution based on a mixture of distilled water, absolute ethanol and hydrochloric acid as catalyst. The corresponding TEOS:ethanol:water molar ratio was 1:18:5. Additionally to the different SiO₂ antireflective coatings studied, different sintering processes of this third constituent absorber layer at 500°C (blower or oven, 5-30 minutes) were analysed.

Regarding the durability tests, the condensation ageing experiment was performed in a Q.U.V. weathering chamber where the samples were exposed to constant condensation at 40°C during 150, 300 and 600 hours meanwhile the thermal stability test was carried out in a conventional circulating air furnace where the samples were first heated at 250°C for 200 hours and then at 300°C for 200, 400, 600 and finally 800 hours. Both ageing experiments were fulfilled following the procedure developed by the international standard ISO 22975-3 (2014).

In order to evaluate the possible degradation of the samples, optical measurements were performed before and after different testing time intervals to calculate the following parameters:

- Solar absorptance (α_s), which was calculated as specified in the standard procedure (UNE 206009:2013) by using the direct AM1.5 solar spectrum from ASTM G173-03 in the 0.3-2.5 μm range and the hemispherical reflectance spectra of the samples recorded from 0.3 to 2.5 μm . The equipment used for the hemispherical reflectance measurements was a UV-VIS-NIR Perkin-Elmer LAMBDA 950 double beam spectrophotometer equipped with a 150 mm Spectralon[®] coated integrating sphere. The associated measurement uncertainty was 1%.
- Thermal emittance (ε_T , 100°C), which was calculated by using the hemispherical IR-reflectance spectra recorded from 2.5 to 17 μm at room temperature and the black body spectrum at 100 °C. A Perkin Elmer Frontier FTIR spectrophotometer equipped with a diffuse gold-coated integrating sphere was used. The accuracy of the reflectance data was estimated to be 2% for the FTIR-spectrophotometer.
- Performance criterion function (PC), which shows the changes in performance of an absorber surface in terms of solar absorptance and thermal emittance (Eq.1)

$$PC = - \Delta\alpha_s + 0.50 \Delta\varepsilon \leq 0.05 \quad (\text{eq.1})$$

where: $\Delta\alpha_s$ is the change in the solar absorptance: $\Delta\alpha_s = \alpha_{s,t} - \alpha_{s,i}$, ($\alpha_{s,t}$ is the value of the solar absorptance at the actual testing time and $\alpha_{s,i}$ is the initial value of solar absorptance) and $\Delta\varepsilon_{T,100}$ is the change in the thermal emittance: $\Delta\varepsilon_{T,100} = \varepsilon_t - \varepsilon_i$ (ε_t is the value of the thermal emittance at the actual testing time and ε_i is the initial value of thermal emittance). This parameter establishes that an absorber can be considered qualified or suitable only if after the test $PC \leq 0.05$, according to standard ISO 22975-3 (2014).

An optical microscope Leica DM4 M was used to study layers degradation.

3. Results and discussion

3.1. Effect of the AR SiO₂ coating and the sintering conditions on the optical parameters

The preparation process for the SiO₂ solutions determines the structure of the films of the coatings. Reflux and high temperature conditions allow obtaining high coating densities by controlling the degree of hydrolysis and the condensation rate. Both kinds of AR silica coatings as third layer (high-density silica A1 or silica prepared without reflux system A2) and different sintering conditions can alter the hemispherical reflectance spectra of the samples and therefore the optical properties of the selective absorber.

Figure 1 shows the variations observed in the reflectance curve shape of the samples (a) CuMnO_x/FeMnCuO_x/A1 and (b) CuMnO_x/FeMnCuO_x/A2 by using different sintering conditions of the silica layer. In Figure 1a), it can be observed that the samples whose third layer (high-density A1) was sintered in the oven for both 15 and 30 minutes reached higher values of reflectance in the second maximum (from 700 nm to the absorption edge) than the samples whose silica layer was sintered in the blower. Also, a shift of the absorption edge to higher wavelengths and a reflectance decrease in the NIR range were observed for these absorbers whose SiO₂ layer was sintered in the oven. Specifically, as far as the absorption edge position is concerned, it is observed that this absorption edge is positioned around 1600 nm for both samples whose dense silica layer was sintered in the oven while for the samples whose SiO₂ layer was sintered in the blower, the absorption edge is registered at 1450 nm. Additionally, focusing on both sintering times studied in the oven, it was noted that as the sintering time increases the second maximum reached slightly higher values of reflectance; being also accompanied by a reflectance decrease in the NIR range.

In counterpart, fewer variations were observed for the absorbers whose A2 antireflective coating was used as third layer. In fact, no differences were appreciated between sintering the silica layer in the blower or oven for 15 minutes. Figure 1b) corroborates that both samples remained identical and maintained the same curve shape. Nevertheless, clear variations were identified for the samples whose A2 layer was sintered in the oven for 30 minutes. Concretely, based on the hemispherical reflectance spectra displayed in Figure 1b), it can be seen that a longer sintering time in the oven implies an increase of the second maximum (going from 5.3 to 7.3% in reflectance at 1120 nm), a displacement of the absorption edge towards higher wavelengths and a decrease in the NIR range.

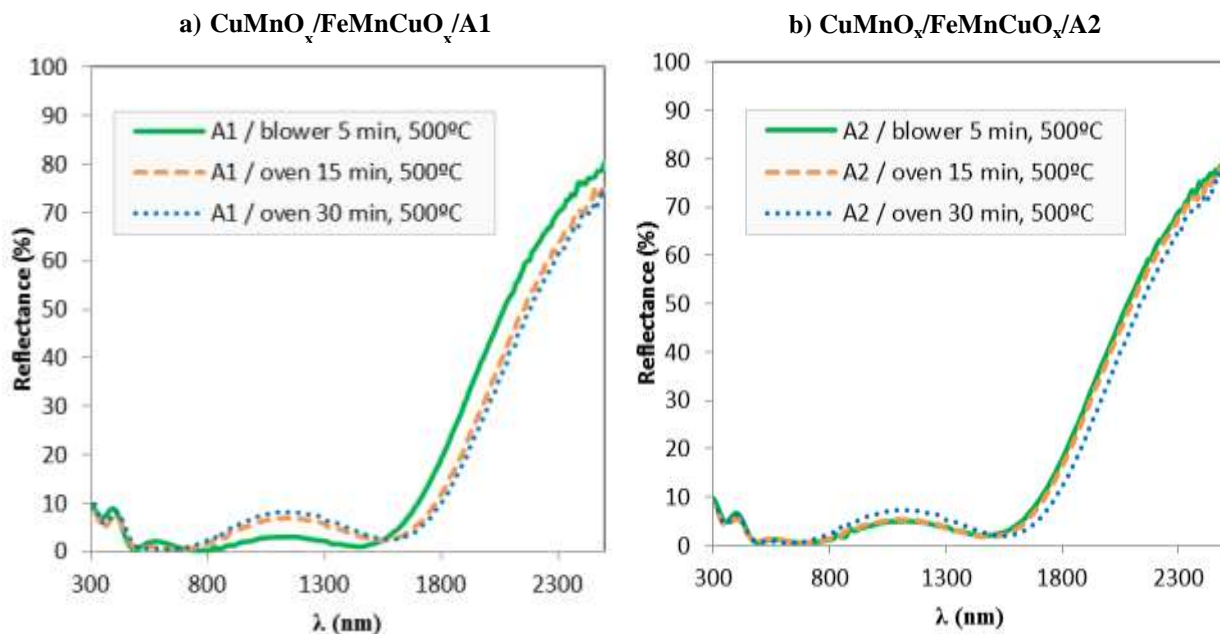


Fig. 1: Variation in the hemispherical reflectance spectra depending on the kinds of SiO₂ antireflective coatings and sintering processes used. Samples whose SiO₂ antireflective coating was the A1 (a) and A2 (b).

The changes observed in the reflectance curve of the samples in the solar range as consequence of the use of different AR coatings and sintering processes of the third constituent absorber layer are closely bound up with the differences in the optical parameters. Table 1 shows the solar absorptance and thermal emittance values obtained for each studied sample. As it can be seen, greater variations in solar absorptance values are perceived than thermal emittance values since the relevant changes in the curve shapes occurred in the solar range, being almost identical the curves in the mid/far IR region. Specifically, in the case of $\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A1}$ samples, a loss of the absorptance value is perceived by sintering the dense silica layer in the oven (0.950-0.953) instead of using the blower (0.957). Regarding the opposite side related to $\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A2}$ samples, a small variation in the solar absorptance value can be remarked. In fact, only a loss of 0.1% of the absorptance value is identified by sintering the A2 layer in the oven for 30 minutes (0.954) instead of using the blower or oven for less time (0.955).

Tab. 1: Variation in the optical parameters of samples with different kinds of silica layer and sintering processes.

Sintering process of SiO_2 antireflective coating	A1		A2	
	Solar absorptance (α_s)	Thermal emittance (ϵ_T)	Solar absorptance (α_s)	Thermal emittance (ϵ_T)
Blower	0.957	0.038	0.955	0.039
Oven, 15 min 500°C	0.953	0.036	0.955	0.037
Oven, 30 min 500°C	0.950	0.039	0.954	0.037

Definitely, by analysing the obtained results it can be concluded that the absorbers whose A1 antireflective coating was used as the third layer were subjected to greater variations with the sintering conditions than the absorbers whose SiO_2 layer corresponded to the A2 antireflective coating.

3.2 Durability study

Apart from studying the consequences resulting from varying the SiO_2 antireflective coating used as third layer and its sintering process in the optical properties of the absorber, thermal stability and condensation tests were carried out separately in order to determine the influence of ageing time at high temperatures and hydrolysis conditions on the durability performance of the absorber. These durability tests were performed in accordance with the international standard ISO 22975-3 (2014).

Regarding the thermal stability test, the accelerated ageing study at high temperatures was performed in a circulating air furnace. Six replicas of each sample whose third layer A1 or A2 was sintered in the blower or oven for 15 minutes were firstly exposed at 250°C for 200h and afterward at 300°C for 200h, 400h, 600h and 800h; being therefore the total duration of the thermal stability test 1000 hours. After each exposure period, the degradation of the samples was analyzed in order to evaluate the performance of both kinds of silica at the sintering processes tested. This degradation study was determined by the optical measurements (solar absorptance and thermal emittance) and the performance criterion parameter (PC). Once concluded the 1000 hours of testing, it was observed that apart from conserving all the samples studied their initial appearance, the absorbers' optical performance was still very good being concretely reduced in all cases less than 5% of its original value. Table 2 shows the average results achieved for the six replicas of each sample analysed after each degradation time interval constituting the thermal stability test. Based on these results, it can be affirmed that all the studied absorber surfaces ($\text{Al}/\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A1}$ and $\text{Al}/\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A2}$) are qualified with respect to their thermal stability regardless of both SiO_2 solutions used and sintering processes of this third constituent absorber layer.

Tab. 2: Average solar absorptance, thermal emittance and PC values calculated before and after each degradation interval for the samples during the thermal stability test.

Samples / SiO ₂ sintering process	Solar absorptance (α _s)	Thermal emittance (ε _T)	PC
CuMnO_x/FeMnCuO_x/A1 (blower)			
Initial	0.957	0.038	
200h/250°C	0.957	0.038	0
200h/250°C + 200/300°C	0.956	0.038	0.0012
200h/250°C + 400h/300°C	0.956	0.038	0.0014
200h/250°C + 600h/300°C	0.956	0.038	0.0014
200h/250°C + 800h/300°C	0.956	0.038	0.0014
CuMnO_x/FeMnCuO_x/A1 (oven, 15 min)			
Initial	0.956	0.038	
200h/250°C	0.956	0.033	0
200h/250°C + 200/300°C	0.953	0.035	0.0014
200h/250°C + 400h/300°C	0.954	0.034	0.0001
200h/250°C + 600h/300°C	0.954	0.034	0.0001
200h/250°C + 800h/300°C	0.954	0.034	0.0001
CuMnO_x/FeMnCuO_x/A2 (blower)			
Initial	0.955	0.039	
200h/250°C	0.955	0.040	0.0007
200h/250°C + 200/300°C	0.951	0.038	0.0027
200h/250°C + 400h/300°C	0.952	0.037	0.0020
200h/250°C + 600h/300°C	0.951	0.037	0.0025
200h/250°C + 800h/300°C	0.950	0.037	0.0035
CuMnO_x/FeMnCuO_x/A2 (oven, 15 min)			
Initial	0.952	0.036	
200h/250°C	0.951	0.038	0.0018
200h/250°C + 200/300°C	0.948	0.035	0.0028
200h/250°C + 400h/300°C	0.950	0.035	0.0018
200h/250°C + 600h/300°C	0.949	0.035	0.0028
200h/250°C + 800h/300°C	0.949	0.035	0.0028

Conversely to the successful results obtained from the thermal stability test, not favorable results were achieved for all the studied samples at the condensation test which implied to keep six replicas of each studied sample at 40°C under constant condensation conditions in the weathering chamber. The extent of degradation of each examined sample was determined after 150h, 300h and 600h of testing by evaluating the aspect of the samples as well as their relative optical measurements. As it can be seen in Table 3, the best data were recorded by the samples whose third layer coincided with the A1 antireflective coating regardless of the sintering process used for this layer. The worst outcomes were obtained for the absorbers whose A2 antireflective layer was applied as third layer. This different behaviour and tendency presented by both types of silica at different sintering processes were expected since the use of different types of silica involves different resulting film structures and the employment of different sintering processes comprises a different burning process of the organic matter in the layer (Khatiri et al., 2014).

As regards the results of resistance to condensed water study of Al/CuMnO_x/FeMnCuO_x/A1 samples, it should be pointed out the different layer degradation that the samples undergone depending on the sintering process used for the A1 layer. In the case of samples whose A1 layer was sintered in the blower, the degradation of the sample surface began to be noticeable only after 600 hours of testing meanwhile the absorbers whose dense silica layer was sintered in the oven (15 and 30 minutes), the corrosion and colour degradation phenomena were perceived since the first 150h-300h of testing; being clearly accented after 600 hours of testing. These visible alterations in the surface of the samples were also reflected on the optical behaviour. Table 3 summarizes the optical parameters as well as the PC values registered for each sample before and after each exposure period. As it can be seen, the three types of Al/CuMnO_x/FeMnCuO_x/A1 absorbers studied presented a slight decrease of the average solar absorptance value and an increase of the average thermal emittance value with the exposure, except for exposure times between 150 and 300 hours in which the values of solar absorptance, thermal

emittance and PC remained unaltered. Otherwise, following with this analysis, it is concluded that the best outcomes are obtained for the samples whose high-density silica is sintered in the blower.

Tab. 3: Average solar absorptance, thermal emittance and PC values calculated before and after each degradation interval for the samples during the condensation test.

Samples / SiO ₂ sintering process	Solar absorptance (α_s)	Thermal emittance (ϵ_T)	PC
CuMnO_x/FeMnCuO_x/A1 (blower)			
Initial	0.957	0.038	
150h/ 40°C	0.955	0.036	0.0010
300h/ 40°C	0.955	0.036	0.0010
600h/ 40°C	0.954	0.038	0.0030
CuMnO_x/FeMnCuO_x/A1 (oven, 15 min)			
Initial	0.953	0.035	
150h/ 40°C	0.950	0.039	0.0055
300h/ 40°C	0.950	0.039	0.0055
600h/ 40°C	0.945	0.042	0.0113
CuMnO_x/FeMnCuO_x/A1 (oven, 30 min)			
Initial	0.950	0.039	
150h/ 40°C	0.945	0.039	0.0051
300h/ 40°C	0.945	0.039	0.0051
600h/ 40°C	0.935	0.040	0.0145
CuMnO_x/FeMnCuO_x/A2 (blower)			
Initial	0.955	0.039	
150h/ 40°C	0.952	0.041	0.0036
300h/ 40°C	0.952	0.041	0.0036
600h/ 40°C	0.942	0.049	0.0181

Despite the variations observed in the optical properties and aspect of the Al/CuMnO_x/FeMnCuO_x/A1 absorbers, all these samples maintained the typical selective absorber curve shape at the end of the ageing test and reached a well below PC value of $PC \leq 0.015$. Therefore, based on these results, it can be concluded that all the Al/CuMnO_x/FeMnCuO_x/A1 absorbers studied, regardless of the sintering process of the A1 layer, are qualified according to the standard ISO 22975-3 (2014) with respect to their resistance to condensed water.

Regarding the condensation accelerated ageing study of samples whose third constituent absorber layer was A2, it should be highlighted the influence of the sintering process of the A2 layer on the durability performance of the absorber. Not all the sintering processes tested for the A2 layer achieved acceptable results. In fact, good results were obtained for samples whose A2 layer was sintered in the blower meanwhile disappointing conclusions were reached for samples whose A2 layer was sintered in the oven.

In relation to the Al/CuMnO_x/FeMnCuO_x/A2 samples whose silica layer was sintered in the blower, a degradation associated to corrosion and washing away of the silica layer began to be noticed after the first 300 hours of testing. These degradation phenomena reached pronounced effects at the end of the accelerated ageing test, i.e. after 600 hours of testing. Figure 2 shows photographs of the process of degradation undergone by the sample under study as the condensed test proceeds.

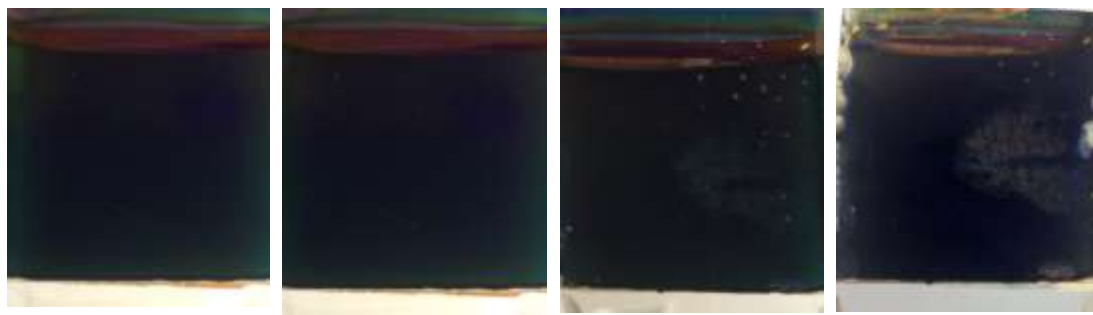


Fig. 2: Photographs of the Al/CuMnO_x/FeMnCuO_x/A2 (blower) selective absorber before (a) and after exposure to condensation at 40°C after 150 hours of testing (b), 300 hours (c) and 600 hours (d).

Each degradation in the aspect of these samples was accompanied by an alteration of the final reflectance spectra of the samples (keeping at all time the typical selective absorber curve shape) and in turn the optical properties. Figure 3 represents the variations observed in the hemispherical reflectance spectra of Al/CuMnO_x/FeMnCuO_x/A2 (blower) samples before and after each studied ageing step in the weathering chamber. By analysing the reflectance spectra, it is seen that the highest variations were registered for the samples which were subjected to a longer time in the weathering chamber (600 hours), remaining almost identical the curve shape of the samples before and after 300 hours of testing. Focusing on the trend followed by the reflectance spectra recorded in the solar wavelength range along the condensed test, it can be established that as the ageing test proceeds, a slight reflectance decrease in the UV-VIS wavelength range is achieved with a slight displacement of this first maximum (400-430 nm) towards longer wavelengths. This variation related to the first maximum is also accompanied by an increase of the second maximum (700 nm until the absorption edge) and a displacement of the absorption edge towards longer wavelengths and higher values of reflectance. A significantly decrease in the NIR range is also produced being clearly confirmed this occurrence in the reflectance spectra recorded from 0.3 to 17 μm wavelengths. These variations lead to important differences in thermal emittance values (Table 3).

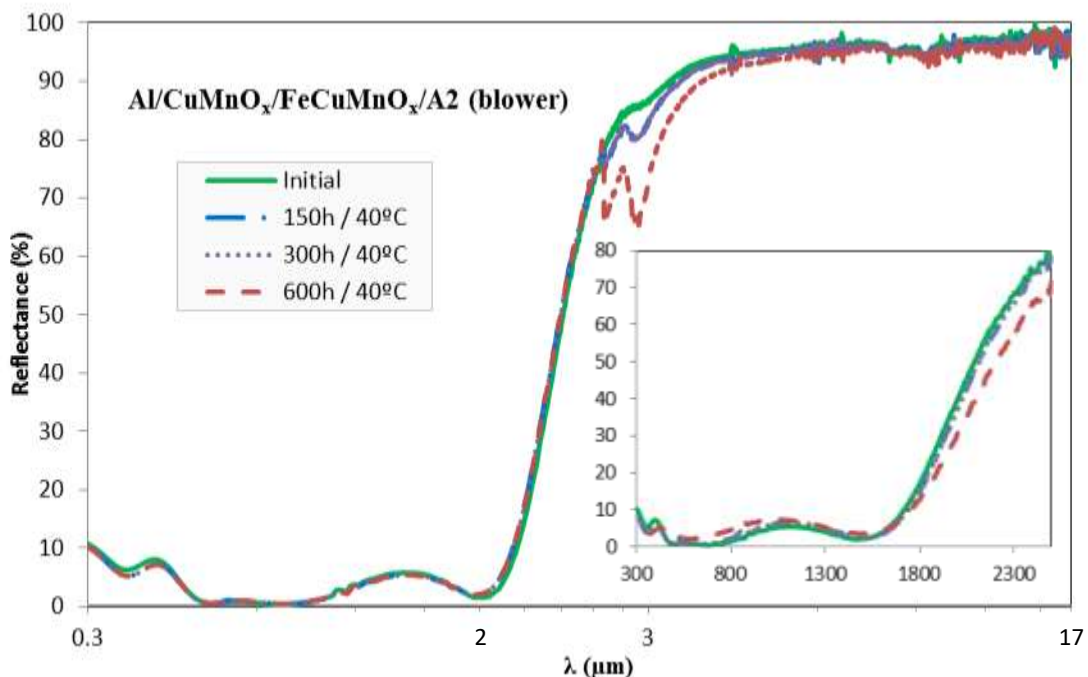


Fig. 3: Variation of the hemispherical reflectance spectra for wavelengths from 0.3 to 17 μm of Al/CuMnO_x/FeMnCuO_x/SiO₂ (blower) samples before and after each ageing step in the weathering chamber and a zone amplification of the solar range (inset).

Based on the results shown in Table 3, it can be seen that the average solar absorptance value of the Al/CuMnO_x/FeMnCuO_x/A2 (blower) sample decreases from 0.955 (un-aged) to 0.942 (after 600 hours at 40°C) as the time of exposure proceeds and the average thermal emittance value increases from 0.039 (un-aged) to 0.049 (after 600 hours at 40°C). Nevertheless, even though the relevant alterations observed for the samples

after 600 hours of testing, it should be highlighted that these samples presented a well below PC value, $PC \leq 0.018$, and conserved the typical selective absorber curve shape at the end of the ageing test. Therefore, based on these results, it can be concluded that the absorbers whose A2 layer was sintered in the blower are qualified according to the standard ISO 22975-3 (2014) with respect to their resistance to condensed water.

However, different results were obtained for samples whose A2 silica layer was sintered in the oven for 15 and 30 minutes. These samples underwent a strong degradation since the first 150 hours of testing; resulting covered by many white spots due to the oxidation of the aluminum substrate and losing the typical absorber colour given the degradation of the silica layer. The worst results were registered for the Al/CuMnO_x/FeMnCuO_x/A2 samples whose silica layer was sintered in the oven for 30 minutes. In this way, a detailed study focused on these samples is shown.

Figure 4a) and Figure 4b) show photographs of the degradation phenomenon of the Al/CuMnO_x/FeMnCuO_x/A2 (oven, 30 minutes) sample before (a) and after (b) the first 150 hours of testing at 40°C. By comparing both images, it can be deduced that the initial coating appearance of the sample with an excellent uniformity and a minimum number of defects (Figure 4a) disappears after the first 150 hours of testing (Figure 3b) given its degradation.

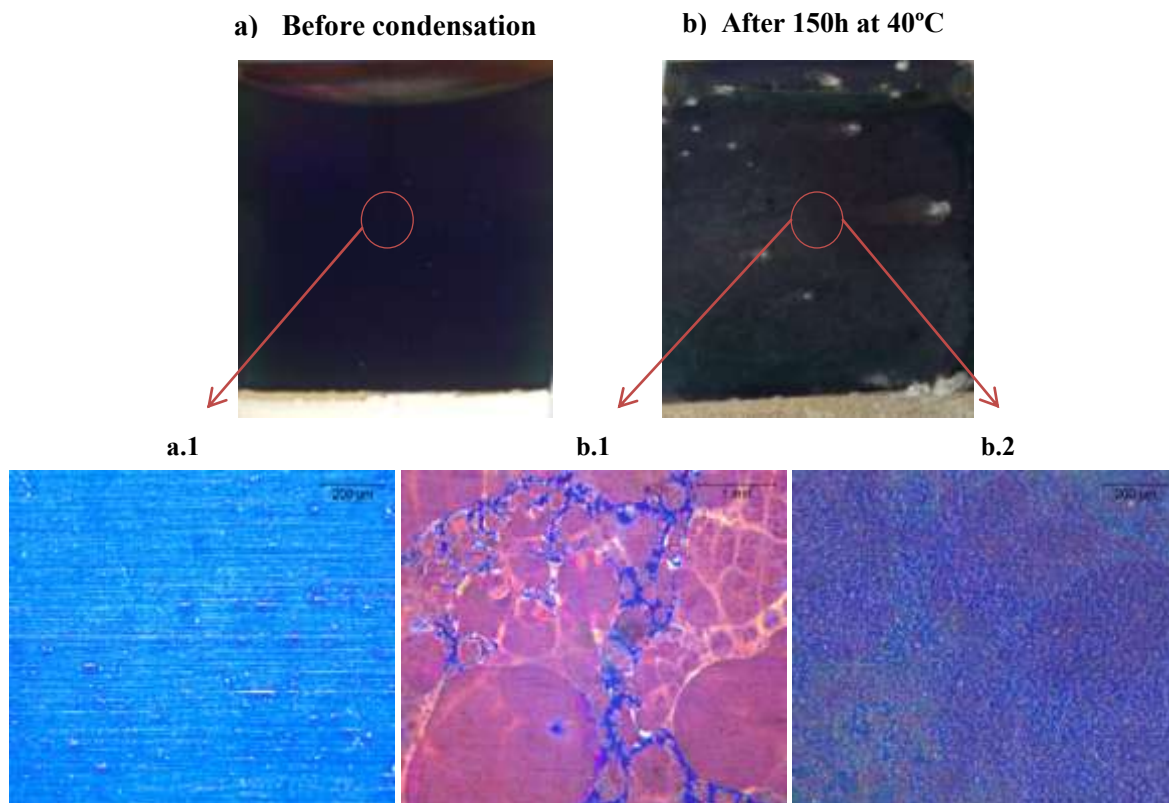


Fig. 4: Photographs of Al/CuMnO_x/FeMnCuO_x/A2 samples whose silica layer was sintered in the oven before (a) and after the first 150 hours (b) of exposure to condensation at 40°C. Images a.1 (x100), b.1 (x25) and b.2 (x100) correspond to the analysis carried out with the optical microscope.

Additionally, in order to understand the degree of degradation to which the Al/CuMnO_x/FeMnCuO_x/A2 (oven) samples are subjected during the condensation test, images of the samples were obtained with the optical microscope. The surface uniformity of the un-aged absorber observed in Figure 4a) was confirmed by analyzing Figure 4a.1), which clearly shows a uniform colour with some lines that come from the machining process for obtaining the aluminum substrate. However, as it can be seen in Figure 4 b.1, the initial coating uniformity disappears after 150 hours of condensation testing being identified two different areas; associating the blue colour to the area of the sample where the A2 layer has not been strongly affected by constant condensation conditions and the red-pink colour to the area of the sample where the A2 layer has been devoid and therefore degraded. Besides, a supplementary reasoning was reached by analysing the sample at a greater magnification

(x100) in the optical microscope. Concretely, focusing on Figure 4b.2 it is leded the conclusion that even the area of the sample which had apparently conserved to a larger extent the integrity of the silica layer in Figure 4b.1) was really degraded after 150 hours of testing since the coating surface was full of white spots, presenting a non-uniform aspect.

The evident alterations observed in the aspect of $\text{Al/CuMnO}_x/\text{FeMnCuO}_x/\text{A2}$ samples whose A2 layer was sintered in the oven were also accompanied by the loss of the typical selective absorber curve shape and the drop of the solar absorptance value. These results demonstrated that the optical degradation was correlated with the visual changes observed. Figure 5 shows the variations registered in the hemispherical reflectance spectra of the absorbers whose A2 layer was sintered in the oven for 15 minutes (a) and 30 minutes (b) since the first 150 hours of testing in the weathering chamber.

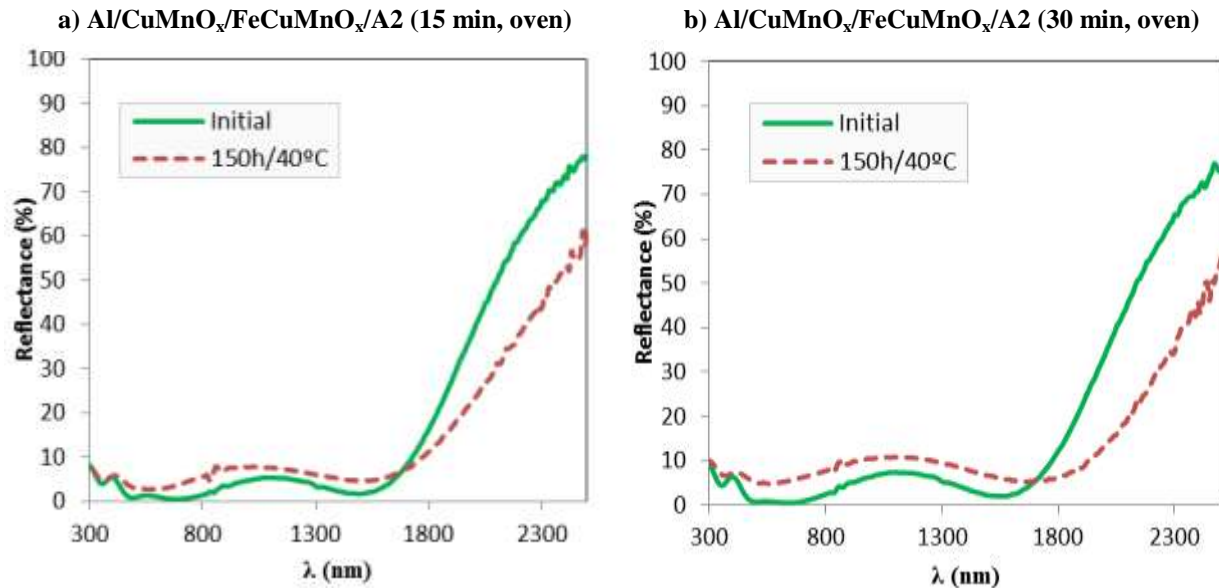


Fig. 5: Variations in the curve shape of the absorbers whose A2 layer was sintered in the oven for 15 minutes (a) and 30 minutes (b) after 150 hours of testing under constant condensation at 40°C in the weathering chamber.

A drop in the solar absorptance value to 0.94 was registered for the absorbers whose A2 layer was sintered in the oven for 15 minutes and 0.90 for the absorbers whose A2 was sintered in the oven for 30 minutes. Both samples presented a $\text{PC} \leq 0.05$ after the first 150 hours of condensation testing. However, the totally loss of the typical selective absorber curve shape of the samples whose layer was sintered in the oven during both tested times forced to stop the condensation test for these samples. Therefore, based on the results reached, it is established that the $\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A2}$ absorbers whose A2 layer was sintered in the oven, regardless of the time of sintering, are not qualified for the condensation test.

Definitely, excluding the $\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A1}$ absorbers in their entirety and the $\text{CuMnO}_x/\text{FeMnCuO}_x/\text{A2}$ absorbers whose A2 layer was sintered in the blower which were qualified with respect to the condensation test with a $\text{PC} \leq 0.02$ after 600h of testing, the rest of the absorbers whose A2 antireflective layer was sintered in the oven, failed the condensation ageing test since they have undergone a strong degradation after the first 150 hours of testing at 40°C. In this way, based on the global results obtained, it can be clearly pointed out that the dense structural silica coating degraded significantly slower and less aggressively than the non-dense silica coating.

4. Conclusions

The performance of the SiO_2 AR coatings was evaluated as it can limit the lifetime performance of the absorber. Concretely, the effect of using two kinds of SiO_2 antireflective coatings and different sintering processes of this third constituent absorber layer on the optical properties and the SiO_2 ability to protect the integrity of the absorber after long term durability tests were studied.

Different conclusions were achieved by comparing the results obtained from both components of the durability test confirming the general trend which considers much more aggressive the condensation tests than the thermal stability tests. The results indicated that the typical testing conditions of the thermal stability test have not enough influence on the optical properties of the samples studied being in this way all of them qualified regardless of the SiO₂ antireflective coating used as well as the sintering process of this layer. However, in the case of the condensed accelerated ageing test, not all tested samples withstood the condensation conditions. The results obtained revealed that these testing conditions affected differently the samples studied. Concretely, two absorber types whose A2 antireflective layer was sintered in the oven (15 and 30 minutes) failed the ageing test after the first 150 hours of testing. Although these samples presented an accepted PC criterion ($PC \leq 0.05$) once concluded the first 150 hours of testing, they cannot be qualified according to the international standard ISO 22975-3 since they underwent such a strong degradation that they lost the typical selective absorber curve shape. The other absorbers, which correspond to CuMnO_x/FeMnCuO_x/A1 in its entirety and CuMnO_x/FeMnCuO_x/A2 whose A2 layer was sintered in the blower, passed successfully the PC criteria and were qualified according to ISO 22975-3 with respect to the condensation test.

Based on all the results obtained along this work, it can be confirmed that the methodology used for the preparation of the SiO₂ antireflective coating as well as its sintering process are determinant regarding the ability of the silica layer to withstand, in greater or lesser way, the outdoor conditions. The best results obtained by the CuMnO_x/FeMnCuO_x/A1 absorbers corroborated that the high-density silica layer acquires a better film structure than the silica layer prepared without a reflux system. Concretely, these successful results can be attributed to the sol-gel chemistry process with which the dense silica layer has been prepared; due to the greater layer compaction obtained for the A1 antireflective coating taking into account the larger polymeric chains which are typically obtained by the sol-gel process.

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