

DURABILITY OF ALUMINIUM BASED SOLAR SELECTIVE ABSORBERS UNDER CONDENSED WATER

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ABSTRACT

Sustainable building technology requires the use of solar collectors for heating and cooling purposes. The collectors' efficiency is mainly influenced by the solar absorber performance. Besides the optical properties of the absorber coating, i.e. high absorption of the incident solar radiation and low heat emission, the degradation due to environmental factors should be considered when designing solar absorbers. However, there is a lack of knowledge on the degradation mechanisms. The current standard methodology from ISO 22975-3, created within TASK 10 IEA Solar and Heating Programme only considers the optical degradation. This study focuses on the performance and durability of eight types of aluminium multi-layered absorbers. The combined effect of high humidity (95% RH), condensation and temperature (40°C and 60°C) was studied. The test samples were measured after different testing time intervals to assess the surface/interface (TEM), chemical (EDX) and optical modifications (UV-Vis-NIR and FTIR spectroscopy). The results revealed that the tested conditions are not strongly influencing the optical properties (solar absorptance and thermal emittance) in the case of the samples with anti-reflective layer and/or humidity protection barrier. All these types are qualified according to ISO 22975-3. However, strong colour modifications, layers alteration and chemical composition changes are recorded. The colour stability of the absorber should be a requirement, especially for architectural integration of solar collectors. Moreover, this study has shown that for modern aluminium based coatings, the predominant degradation process is not the formation of aluminium hydroxide, but the reduction of the antireflective layer thickness.

Keywords: accelerated test procedure, lifetime assessment, spectral selectivity, aluminium based solar selective absorbers, degradation mechanism

INTRODUCTION

The research priorities established by the new EU Framework Programme Horizon 2020 are related to foster clean and efficient energy, especially solar energy. Heat generation for domestic or industrial purposes requires almost 50 % of the total energy consumption in Europe. Using solar-thermal systems can help to decrease the fossil fuels consumption and the pollution, also significantly contributing to the EU's energy security strategy.

Considering the components of a solar collector (glazing, absorber, heat insulation, casing), the solar absorber is drastically influencing the collectors' efficiency. Efficient solar absorbers with high absorption (α_s) of the incident solar radiation and low heat emission (ϵ_t) are already reported in many papers and reviews which synthesize the state of the art [1, 2]. Nevertheless, the long term stability of the solar absorber materials should be assessed, as the manifold micro-climatic conditions can significantly deteriorate the material's performance. The minimum lifetime of a solar thermal system is estimated to be 20-25 years. Thus, the

materials should maintain the optical performance within this period [3]. Most of the papers report only the (initial) optimized optical values and the durability is rather neglected.

The main degradation processes are due to high temperature, high humidity and water condensation, and/or sulphur dioxide as an airborne pollutant [4]. The method used for assessing the resistance to the factors mentioned is described in ISO 22975-3:2014 part 3 and it was developed about 20 years ago. The new and efficient solar absorbers are generally based on multilayers with complex degradation mechanisms. Moreover, aluminium and stainless steel absorbers are about to replace the formerly predominant copper in the worldwide market because of strongly increased copper prices. There is a lack of knowledge on the lifetime assessment of these solar selective absorbers and only a few reports on this topic exist [5, 6]. The stability to temperature of some aluminium based absorbers with and without anodized layer was evaluated by M. Kotilainen et al. [5]. The influence of a thin Al IR reflective layer on the absorber's durability was also investigated. In the case of humidity, there are even fewer reports [6], most of the research was done in the framework of Task X.

The paper presents the combined effect of high humidity (95% RH), condensation and temperature (40-60°C) for different selective coatings which are commercially available or under development. The test samples were measured after different testing time intervals to assess the surface/interface (TEM), chemical (EDX) and optical modifications (UV-Vis-NIR and FTIR spectroscopy).

EXPERIMENTAL DETAILS

Different modern solar selective absorbers obtained by physical vapour deposition were tested in high humidity and condensation at 40°C, or at 60°C and 95% RH humidity. The report codes denote the following types of absorbers: type 1: standard product, deposited on modified aluminium substrate, type 2: standard product, type 3: standard product, deposited on thin eloxal layer type 4: electrochemically anodized Al, optically dense Al layer, modified absorber layer, type 5: electrochemically anodized Al, optically dense sputtered Al layer, type 6: Al Constellium, no anodization, with chemical passivation layer, type 7: selective absorber with humidity protection layer, type 8: selective absorber without humidity protection layer.

The condensation tests were performed in a climatic chamber (Horstmann HS 220 K 45, volume 0.22 m³) with a cooled sample holder designed according to the recommendation from ISO 22975-3:2014 part 3. The sample temperature was controlled using a thermostatic bath (Lauda RK8 KP). Three samples (5x5 cm) from each type were exposed to high humidity and condensation (HHC) and measured before and after different ageing times.

Optical measurements (Bruker IFS66) were performed to calculate the following parameters: *a) solar absorptance* (α_s) which represents the fraction of solar radiation energy absorbed by the absorber surface, *b) thermal emittance* ($\varepsilon_{t, 100}$) which represents the ratio between the energy radiated (per unit area) by the absorber surface at 100°C and the corresponding energy radiated by a perfect black body at the same temperature, and *c) performance criterion function* which shows the changes in performance of an absorber surface in terms of solar absorptance and thermal emittance (Eq. 1).

$$PC = -\Delta\alpha_s + 0.50 \Delta\varepsilon_{t,100} \leq 0.05 \quad \text{Eq. 1}$$

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 solar absorptance at the actual testing time and $\alpha_{s,i}$ is the initial solar absorptance), and $\Delta\varepsilon_{t,100}$ is the change in the thermal emittance: $\Delta\varepsilon_{t,100} = \varepsilon_t - \varepsilon_i$ (with ε_t - the thermal emittance at the testing time t and ε_i is initial thermal emittance). The average optical values are reported for each sample type.

Microstructural and elemental composition modifications after ageing were studied using a transmission electron microscope (TEM, FEI Talos F200X) equipped with an energy dispersive X-ray spectrometer.

RESULTS AND DISCUSSION

The samples were first visual inspected after each degradation time intervals and then the optical measurements were performed in order to calculate the solar absorptance, thermal emittance and PC values.

Strong colour degradation was observed for most of the samples exposed for longer testing times (1056h) at 60°C and 95%RH (Figure 1). For the samples tested at lower temperature (40°C), even after approx. 1500 h, the colour was unchanged. A pitting corrosion was however observed.

Although the aspect of the samples has changed in some cases dramatically, the absorbers' optical performance was still very good. The performance criterion values were generally very small, even after approx. 1500 h of testing (Table 1). Only the samples without humidity protection barrier have failed after first measurements when the value of the thermal emittance was similar with the one recorded for the uncoated aluminium substrate. Thus, the PC value was higher than 0.3, much higher than the maximum admitted value (0.05) which corresponds to a relative decrease of the annual solar fraction of a typical domestic hot water system by 5%. This type was not further included in the tests.

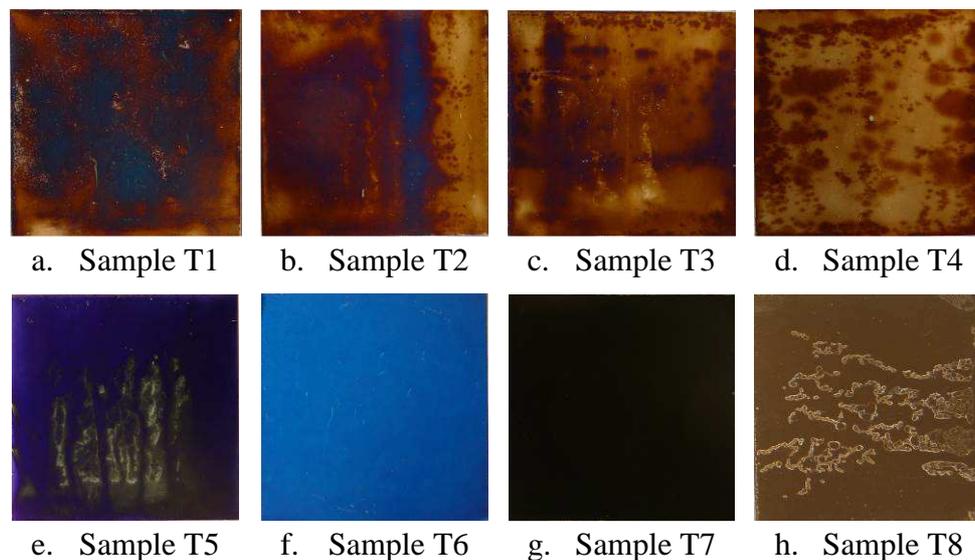


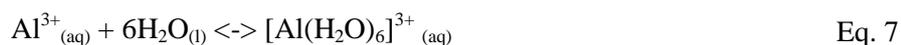
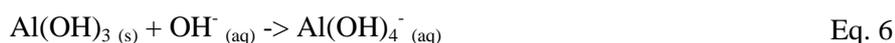
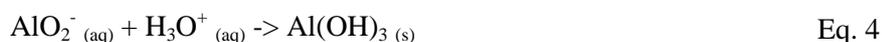
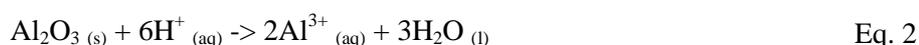
Figure 1: Samples after exposure to condensation and high humidity (60°C, 95%RH) after 1056 h (44 days) of testing (a. - g.), and after 384 hours of testing (h.), respectively.

For the tested aluminium based absorbers, longer testing periods are necessary in order to obtain a consistent change in the optical properties for the calculation of the activation energy based on the Arrhenius plot. After more than 1000 h of testing, no significant variation was obtained. In this case, testing at higher temperature to accelerate the degradation processes might be a solution. However, the hypothesis from Task X was that the degradation is different at higher temperatures due to the formation of more stable aluminium compounds.

Sample	PC values after different testing time intervals at 40°C				PC values after different testing time intervals at 60°C		
	270h	384h	1056h	1464h	384h	816h	1056h
T1	0.012	0.011	0.013	0.012	0.022	0.025	0.012
T2	0.004	0.002	-0.002	-0.003	0.001	0.006	0.007
T3	-0.001	-0.001	-0.003	-0.003	0.000	0.003	0.007
T4	0.008	0.005	0.002	0.000	-0.004	0.007	0.021
T5	-0.001	0.004	0.003	0.003	-0.004	-0.002	0.000
T6	0.000	0.004	0.001	-0.001	0.002	0.009	0.014
T7	0.006	0.006	0.007	0.006	0.004	0.008	0.004
T8	0.380		-	-	0.384	-	-

Table 1: Average PC values calculated after different degradation intervals for the samples tested in high humidity and condensation at 40°C and 60°C with 95%RH.

The possible degradation mechanisms/compounds were further investigated by performing HAADF-STEM (High Angle Annular Dark Field - Scanning Transmission Electron Microscopy) combined with energy-dispersive X-ray (EDX) measurements. The depth composition for the un-aged sample T4 and for the aged sample at 40°C (after 32h) is presented in Figure 3 and in Figure 5. The sample T4 has an anodized aluminium substrate (with the thickness of the anodized aluminium oxide about 140 nm, Figure 2). Two thin metallic layers are used as IR reflectors and diffusion barrier before depositing the Cr based absorbing coating. The antireflective coating is SiO₂ with a thickness of approx. 85 nm. The cross section of the un-aged sample was examined by HAADF-STEM (Figure 2) and it shows a sharp interface between the layers. However, after degradation, the layers and especially the interface between layers are modified (Figure 4) due to diffusion of elements, hydratization and other possible degradation mechanisms. Depth composition measurements were performed by EDX for each individual layer visible on the HAADF STEM image. What is interesting to notice from these depth profiles is that Al and Cr are present at the surface in the as received as well as in the aged sample, with Al slightly increasing in the aged sample. At the surface, different reactions depending on the pH of the environment might occur (Eq. 2-7), with the formation of different (soluble) aluminium compounds.



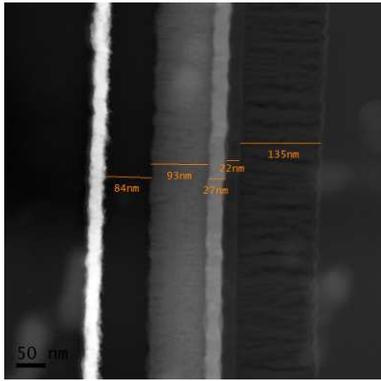


Figure 2: HAADF STEM image of the un-aged sample T4

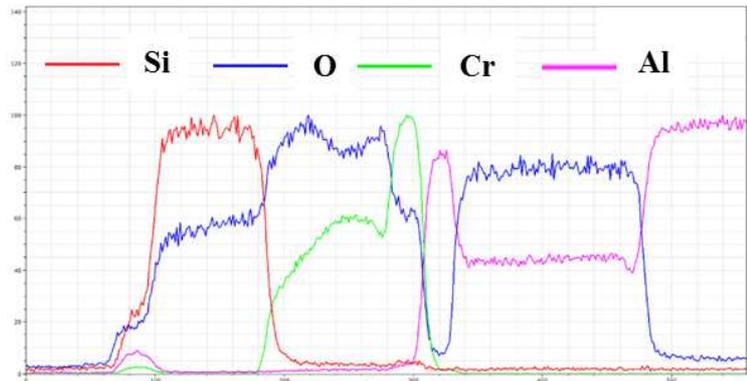


Figure 3: Depth composition for the un-aged sample T4

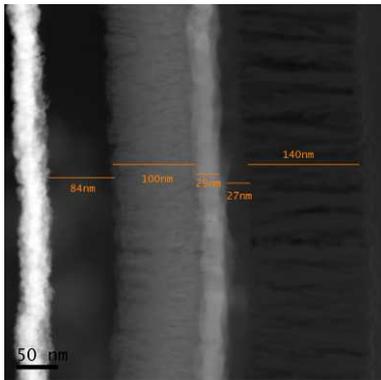


Figure 4: HAADF STEM image of the aged sample T4

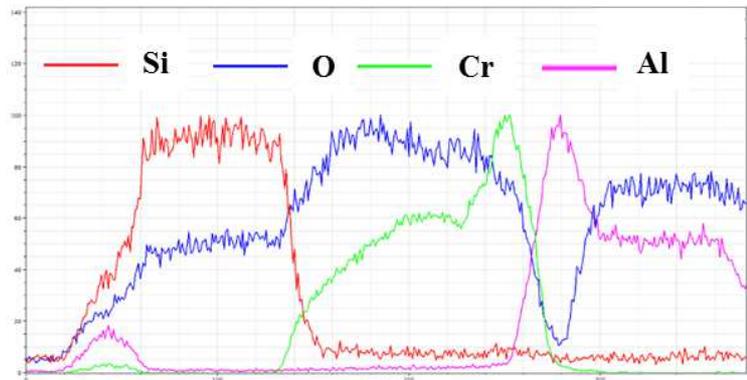


Figure 5: Depth composition for the aged sample T4

Besides diffusion, another mechanism was identified. The modification of the antireflective layer was observed in the UV-Vis-IR spectra. The characteristic band from 1085 cm^{-1} (approx. $9.2\ \mu\text{m}$) which correspond to the Si-O-Si stretching [7] is decreasing in intensity for all the aged samples (Figure 6). In some cases, for example for sample T4 after 1056 h of testing at 60°C is no longer visible (Figure 6). This is in accordance with the spectroscopic measurements performed in the UV-Vis wavelength range. The interference peaks are shifted towards lower wavelengths (Figure 7), indicating film (optical) thinning. Therefore, it is very likely that the SiO_2 film which gives the blue reflection is partially washed away or destroyed.

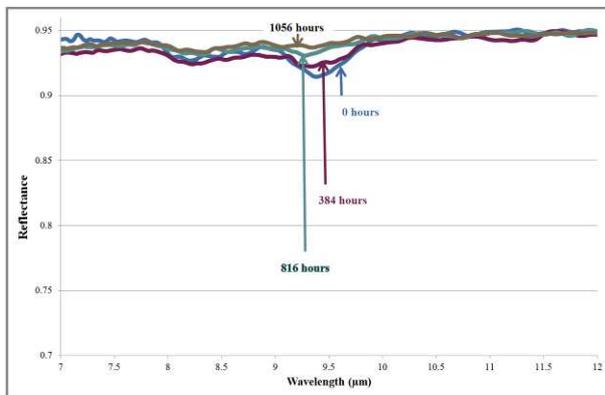


Figure 6: IR spectra (selection) for the un-aged and aged sample at 60°C and 95%RH (sample T4)

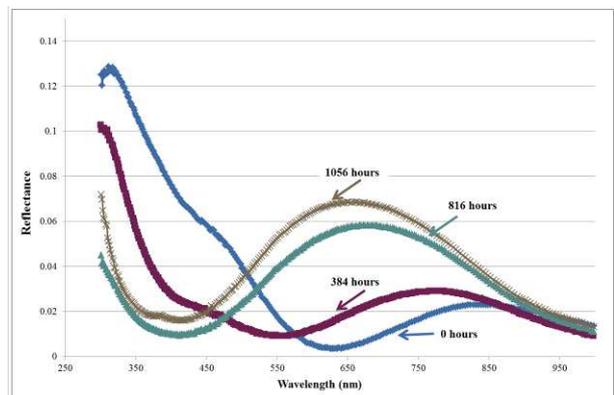


Figure 7: UV-Vis spectra of the un-aged and aged sample at 60°C and 95%RH (sample T4)

CONCLUSION

The combined effect of high humidity, condensation and temperature (40°C and 60°C) was studied for eight types of aluminium based solar selective absorbers. The results indicate that the testing conditions are not strongly influencing the optical properties of most of the samples. Only one absorber type which had no humidity barrier has failed the PC criteria after the first 270h. The other absorber types are qualified according to ISO 22975-3. However, other modifications were recorded, depending on the testing conditions: colour modifications, layers alteration and chemical composition changes. Different degradation/corrosion mechanisms in the tested conditions are proposed.

Although the absorbers were able to maintain their optical performance, the colour changed considerably for the samples tested at 60°C and 95%RH. This is due to the fact that the antireflective layer (SiO₂) which gives the blue reflection was partially destroyed and/or washed away. Especially for architectural integration of solar collectors, the colour stability of the absorber should be a requirement.

For the experiments carried out during the Task X, the main degradation mechanism for aluminium based coatings was the formation of hydroxide, which did not allow testing temperatures above 40°C. This study has shown that the predominant degradation mechanism for modern coatings is different and for this reason is not bound to testing temperatures below 40 °C. In this case, testing at higher temperatures to accelerate the degradation processes and to decrease the testing time might be a solution, but further studies are required.

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