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Durability testing of silvered-glass mirrors

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Abstract

Durability analysis of solar mirrors is attracting attention from Concentrating Solar Power (CSP) developers because guaranties of a suitable optical behavior during the whole service life time are required. To give realistic life time estimations in affordable time, research institutes are investing a lot of effort in developing appropriate accelerated aging tests. In this paper, an extensive test campaign of accelerated aging tests has been performed with silvered-glass mirrors from several manufacturers. Three commercial outdoor-proven products, a not outdoor-proven mirror prototype and two mirrors which showed degradation after only three years of outdoor operation in Spain and Australia have been tested. The accelerated aging tests were conducted for an extended period of time in order to determine the testing time at which the two mirror materials that showed degradation outdoors start to fail under the accelerated conditions. The degradation of the outdoor exposed mirrors is analyzed microscopically and compared to the degradation appearing under accelerated aging. The presented data on accelerated testing represents useful information for standardization of durability testing of solar mirrors.

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Nomenclature	
CASS	Copper accelerated salt spray test
CSP	Concentrating Solar Power
EDX	Energy dispersive X-ray spectroscopy
NSS	Neutral Salt Spray test
PSA	Plataforma Solar de Almería
SEM	Scanning electron microscopy
ρ(660nm;15°;12.5mrad)	Specular reflectance at wavelength 660 nm, incidence angle 15°, acceptance angle 12.5 mrad

1. Introduction

The commonly used reflectors in CSP applications are silvered glass mirrors with a glass thickness of 1 to 4 mm. Solar glass with trace elements (FeO, Fe_2O_3, K_2O, SO_3 etc.) of lower than 5 wt% is used to achieve a high transmission in the entire solar spectrum (280 - 2500nm). Solar glass usually consists of silicon dioxide (SiO_2 69 - 74 wt%), sodium oxide (Na_2O 10 - 16 wt%), calcium oxide (CaO 5 - 14 wt%), magnesium oxide (MgO 0 - 6 wt%) and aluminum oxide (Al_2O_3 0 - 3 wt%) [1]. Thick glass mirrors typically have a thickness of 4 mm offering sufficient mechanical strength against wind loads. Thin glass mirrors, usually of 1 mm glass thickness, require a backing structure to prevent mirror breakage and to provide the concentrating shape. At normal incidence, 4% of the incident sunlight is reflected at the glass-air interface. A thin silver layer of approximate thickness of 150 nm is deposited to the solar glass by wet silver processes. The main component of sunlight is reflected by the silver layer. Usually a 150 nm copper layer is applied on the silver to decelerate silver corrosion (copper acts as sacrificial anode as it has a lower standard electrode potential) and to prevent transmitted UV-light to reach the prime and intermediate coats. The around 30 µm thick primer and intermediate coats contain zinc, magnesium, calcium, barium, sulfur, iron, silicon and lead compounds. The prime coat acts as corrosion preventer and the intermediate coat as diffusion barrier. The top coat contains TiO_2 (Rutil) to prevent UV-radiation from reaching the intermediate coating (see Fig. 1a).

Silver is used for the production of solar mirrors due to its optical properties and rather high ionization potential. However, silver may strongly corrode in presence salts, ozone and pollutants. The corrosion phenomenon of silver under atmospheric conditions is frequently called tarnishing. The tarnishing process of silver depends on many factors, such as pH, humidity, radiation, wind velocity, temperature, nature and concentrations of air pollutants and aerosols, and exposure time. Moreover, it is often noted that silver and silver compounds have strong interactions with sulfur [2]. The increasing concentration of anthropogenic caused corrosive gases such as H_2S, SO_2, CO_2 and O_3 present in urban environments is challenging corrosion scientists. It could be shown that the presence of a strong oxidizer such as ozone increases the corrosion rate of silver if H_2S or SO_2 are present in the ambient atmosphere [3]. Silver corrosion occurs as well indoors, requiring protective paint coatings to prevent tarnishing [4,5]. Alternative methods to protect the metallic silver layer are sol-gel layers, Physical Vapour Deposition (PVD) or Atomic Layer Deposition (ALD) nano-films [6].

2. Materials and methods

Mirror samples from six manufacturers have been subjected to an accelerated aging testing campaign in the OPAC laboratory at the Plataforma Solar de Almería (PSA), a joint research group between DLR and CIEMAT. Samples from outdoor-proven commercial products are referred to as 'A 1- 3'. These samples have the layer construction shown in Fig. 1a. The same accelerated aging tests were additionally conducted with a recently developed and not outdoor-proven mirror which is referred to as 'B 1'. Those samples use only two paint protection layers instead of the usually applied three (see Fig. 1b). Two samples are included in this study, which have shown degradation after two to three years of outdoor operation in locations suitable for CSP applications (Tabenas, Spain, dry desert area and Newcastle, Australia coastal and corrosive site due to coal mining industry closeby). They are

referred to as 'C 1' and 'C 2'. The layer construction of samples 'C 1' follows Fig. 1a, the layer construction of samples 'C 2' follows Fig. 1c. Samples 'C 2' lack of the copper layer as bonding layer between the silver and the prime coat. For accelerated testing, non-aged samples from the same manufacturing batch that the samples from the field were used. They have been stored indoors during the two to three year periods. The tested samples have been cut to a size of 10 x 10 cm from original facets using a conventional glass cutter. All samples contain at least one edge with original edge protection. No conclusions are drawn from corrosion effects at non-protected edges.
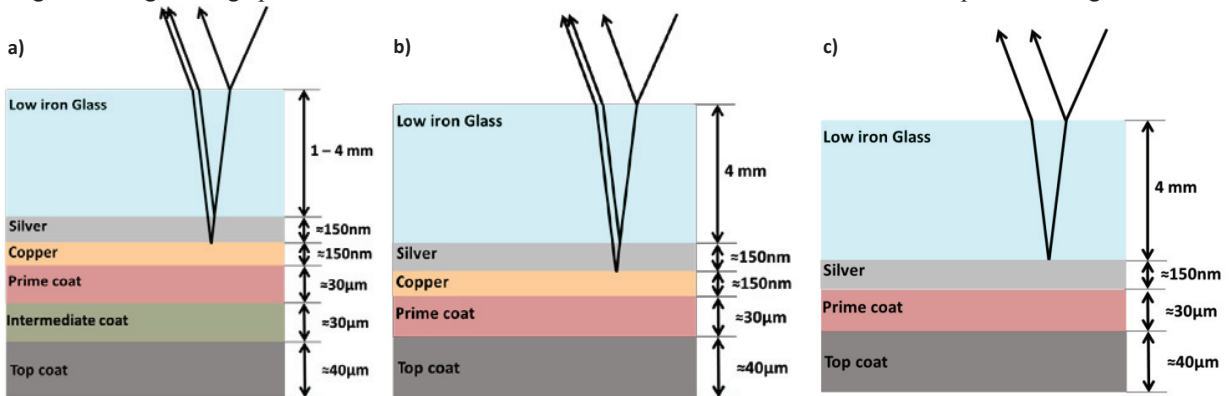

Fig. 1: Layer construction of samples a) 'A 1 – 3' and 'C 1', b) 'B 1', c) 'C 2'

The aim of the accelerated aging testing campaign is to identify those tests which are capable to detect the samples which showed degradation outdoor and to compare the appearance of degradation with the degradation in the climate simulation chambers. Accelerated testing is performed on three glass mirror samples of size 10 x 10 cm². The testing campaign involves: 2000 h of Damp Heat (IEC 62108, Test 10.7), 3000 h of Neutral Salt Spray (NSS, ISO 9227), 2000 h of UV-light and Humidity (ISO 11507), 480 h of Copper Accelerated Salt Spray (CASS, ISO 9227) and 150 Thermal Cycles (IEC 62108, Test 10.8) with Damp Heat.

The Damp Heat test is used to test the resistance against penetration of humidity through the paint coatings at relatively high temperatures. The samples are subjected to a constant climate of $85 \pm 5\%$ relative humidity and $65 \pm 2°C$ in a climatic chamber. The test has been performed during 2000 hours and intermediate measurements have been made every 500 hours. In the NSS test samples are exposed to constant conditions of 35°C with a spray of a NaCl solution (50 ± 5 g/l, pH = 6.5-7.2) at 100% humidity. The amount of the sprayed solution is adjusted to obtain a condensation rate of 1.5 ± 0.5 ml/h on a surface of 80 cm². The UV+Humidity test consists of the following cycle: initially, samples are exposed during 4 hours at 60 ºC to UV-radiation in the wavelength-range of 290-400 nm with a peak emission at 340 nm. The UV dose of one cycle corresponds approximately to one sunny day in Florida. Afterwards, the samples are exposed during 4 hours at 50ºC to condensation (100% relative humidity without irradiation). The total duration of one cycle is 8 hours. It is recommended to expose both, the front and back side of different reflector samples to the interior of the testing chamber. In the CASS test samples are exposed to $50\pm 2°C$ and 100% relative humidity with a constant spray of demineralized water containing 50 ± 5 g/l NaCl. Additionally the solution contains 0.26 ± 0.02 g/l of copper chloride ($CuCl_2$). The pH of the sprayed solution lies between 3.1-3.3 and is adjusted using hydrochloric acid (HCl), sodium hydroxide (NaOH) or sodium bicarbonate ($NaHCO_3$). The resistance to formation of cracks or delamination due to thermal influence is tested with thermal cycling tests. The samples are subjected to 150 cycles from -40°C to 65°C without humidity control prior to performing 2000 hours of damp heat testing with the samples. A more detailed description of the testing conditions can be found in the corresponding standards [7-9] or [10].

The appearance of degradation mechanisms in the different accelerated aging tests are classified microscopically at PSA with a 3D light microscope model Zeiss Axio CSM 700. Additionally, the monochromatic specular reflectance of the mirror samples is monitored in different time intervals throughout the tests using a portable specular reflectometer model 15R-USB, manufactured by Devices and Services. Three reflectance measurements are taken at different positions per sample at a wavelength of 660 nm, with an incidence angle of 15º and an acceptance angle of 12.5 mrad, which is indicated as $\rho(660nm;15°;12.5mrad)$. Scanning electron microscopy (SEM)

analysis of selected samples has been performed at DLR using the scanning electron microscope Gemini Ultra 55, manufactured by Zeiss, with an INCA FETx3 Energy dispersive X-ray spectroscopy (EDX) system and at CSIRO using the EVO MA 15 (Zeiss) with a Sirius SD (Silicon Drift) EDX detector.

3. Analysis of degradation effects on outdoor exposed mirror samples

The samples exposed outdoors showed degradation in the field after only two to three years of service. Sample 'C 1' is a silvered-glass mirror of 1 mm glass thickness which is glued to a backing structure. The mirror is installed in a parabolic-trough collector at the PSA in Tabernas, Spain and shows edge corrosion up to 12 mm after approximately two years of outdoor operation (see Fig. 2). The conducted SEM analysis of a cross section of the edge corrosion revealed that the silver layer close to the edge is completely dissolved. EDX mapping showed that further along the edge round silver chloride particles were found as corrosion product (see Fig. 3 d). Delamination occurs in the glass-silver interface. Accelerated testing was performed without the collector backing structure and adhesive.

Fig. 2: Photographs of edge corrosion of material 'C 1' during outdoor operation of approximately 2 years at PSA, Tabernas, Spain.
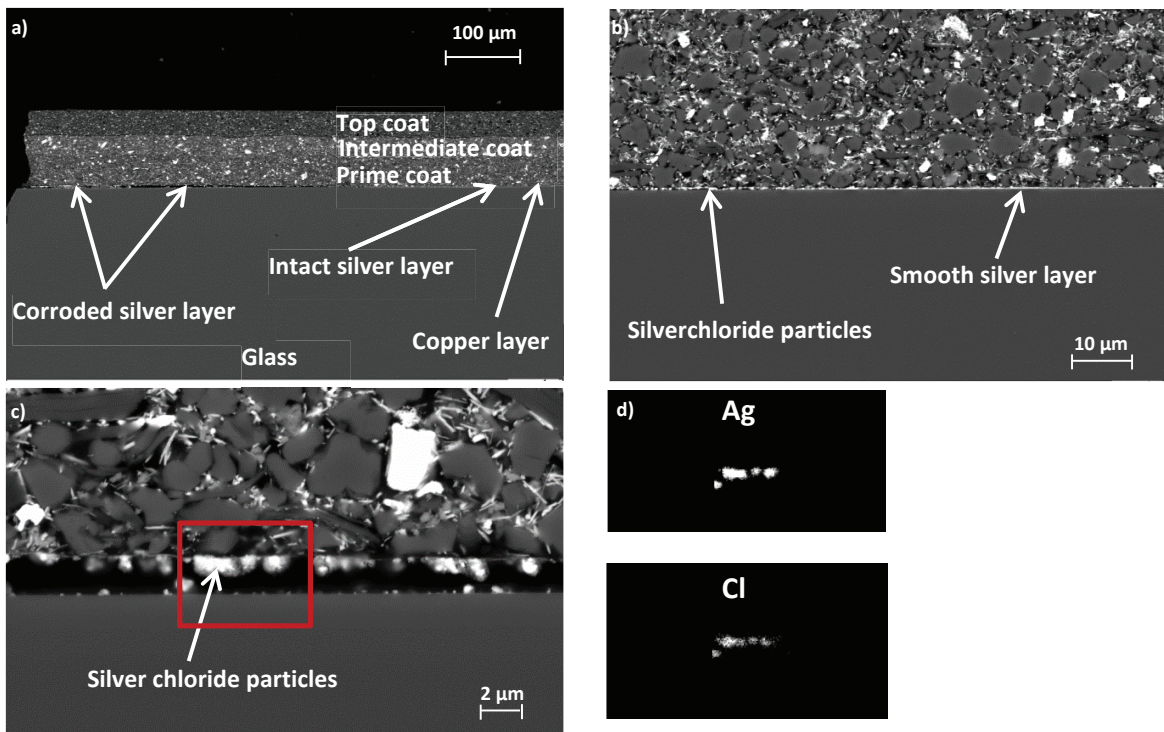

Fig. 3: SEM analysis of material 'C 1' after outdoor operation of approximately 2 years at PSA, Tabernas, Spain. a) cross section of edge corrosion, edge is shown left; b) silver corrosion at end of edge corrosion; c) detail of silver corrosion showing silver chloride particles as corrosion product, d) EDX mapping showing that Ag and Cl are found in identical locations.

Sample 'C 2' is a silvered-glass mirror of 4 mm glass thickness which was approximately three years in operation in the heliostat field of CSIRO in Newcastle, Australia. It consists of a reflective silver layer which is protected by only two paint layers (see Fig 5 top left). An EDX line scan revealed that the mirror lacks the usually employed copper layer which acts as UV protection and bonding layer between the silver and the paint layers. The mirror showed several pitting corrosion spots of diameters up to 29 mm, with an average diameter in the range 6 – 8mm (see Fig. 4). EDX mapping of the cross section revealed the presence of chlorides and sulfates within the corroded area. Pinholes in the top coat have been found by SEM inspection from the back side (see Fig.5 lower right). The
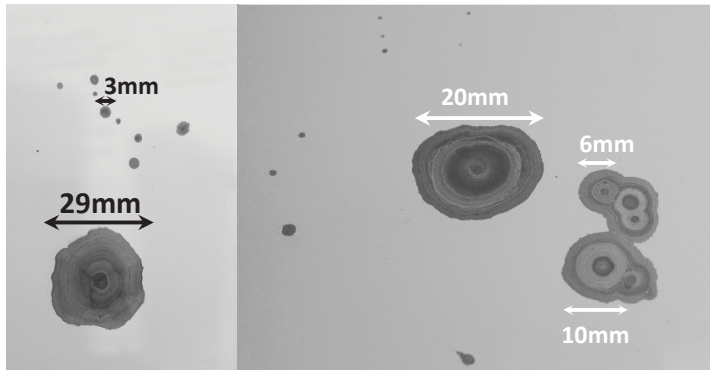

Fig. 4: Photographs of material 'C 2' during outdoor operation of approximately 3 years at CSIRO, Newcastle, Australia.
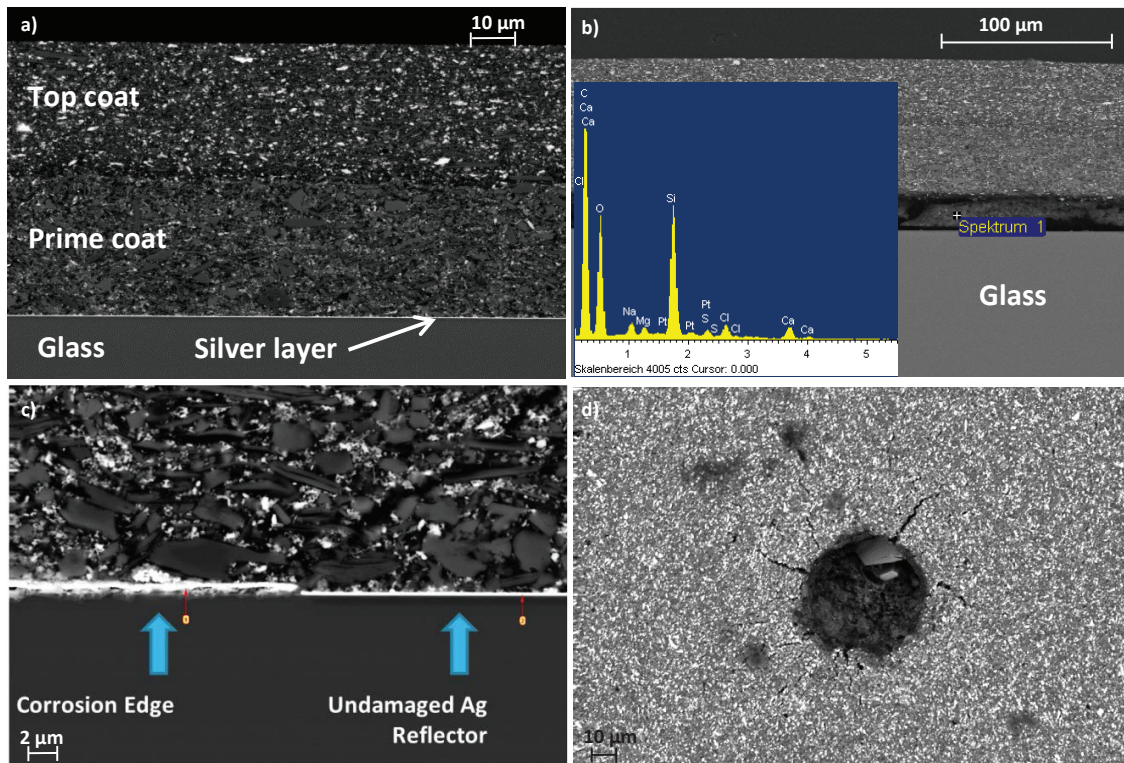

Fig. 5: SEM analysis of material 'C 2' after outdoor operation of approximately 3 years at CSIRO, Newcastle, Australia. a) layer structure of non-degraded mirror area; b) cross section trough local corrosion spot, the EDX analysis shows presence of chloride in the delamination gap; c) detail of silver corrosion at edge of spot; d) top view of pinhole in top coat.

pinholes from the back side could be associated to the silver corrosion from the front side. The cross section analysis trough the corrosion spot revealed that delamination occurred in the silver-paint interface, which is probably due to the lack of the copper layer or due to localized defects in the paint layer.

4. Accelerated aging

Depicted in Fig. 6 is the evolution of the specular reflectance of the six tested material types under accelerated aging. The highest decays are measured after 3000 hours of NSS testing. Almost no optical degradation was measured after 480 hours of CASS testing and after 2000 hours of UV+humidity testing. Only the 'B 1' samples exposed with the back paint layer towards the UV-lamps showed considerable optical degradation. Microscopically there are many small corrosion spots visible (see Fig. 9 in section B1 and UV+Humidity). After 150 thermal cycles most of the samples showed cracks in the paint layers at unprotected edges which were a starting point for corrosion in the posterior damp heat test. Importantly, no cracks were detected at originally sealed edges.

After 500 hours of damp heat and NSS testing and after 1500 hours of UV+Humidity testing first signs of glass corrosion can be appreciated on samples from different manufacturers. The glass corrosion increments severely with time for some samples, especially for 'A 1' in the NSS test (see Fig. 7), where specular reflectance decay is mainly due to scattering and absorption effects at the corroded glass rather than a degradation of the silver layer.
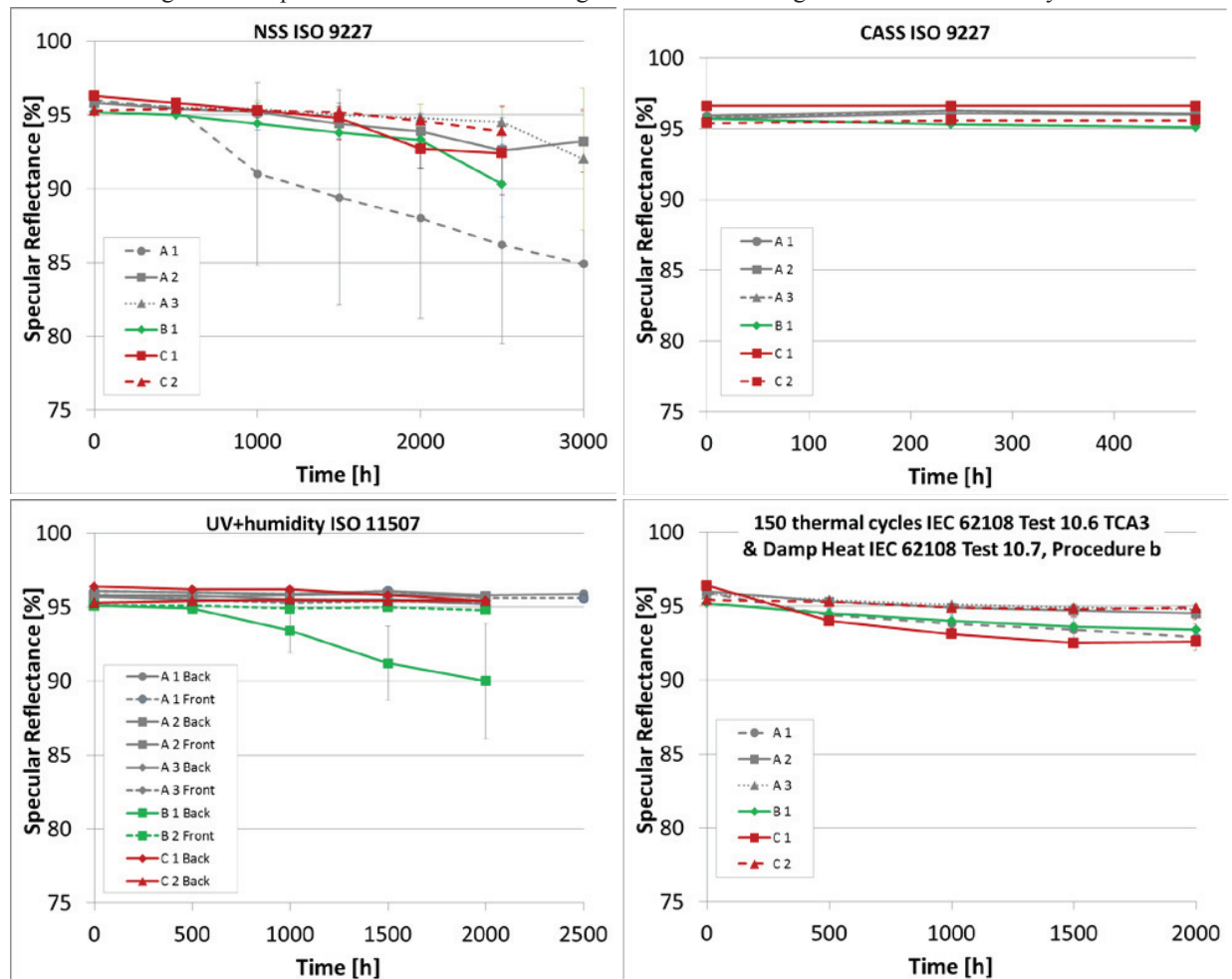

Fig. 6: Specular reflectance ρ(660nm;15°;12.5mrad) variation as function of time in different accelerated aging tests

Fig. 7: a and b) Glass corrosion on 'A 1' samples after 3000 hours of NSS testing; c) Microscopic view of glass surface

The detected edge corrosion observed outdoors of samples 'C 1' was reproduced by thermal cycling testing in combination with 2000 hours of damp heat (compare Fig 8 to Fig 3). A top view on the glass surface from which the paint layers delaminated revealed the presence of round shaped copper containing particles and remaining rests of silver by EDX analysis. The copper particles seem to deposit directly on the glass surface where the silver is corroded. The diffusion process of copper into the silver layer indicates that the testing temperature of 65°C might be inappropriate to reproduce the silver corrosion mechanism realistically. Copper diffusion into the paint layer has also been reported during NSS testing in [11].
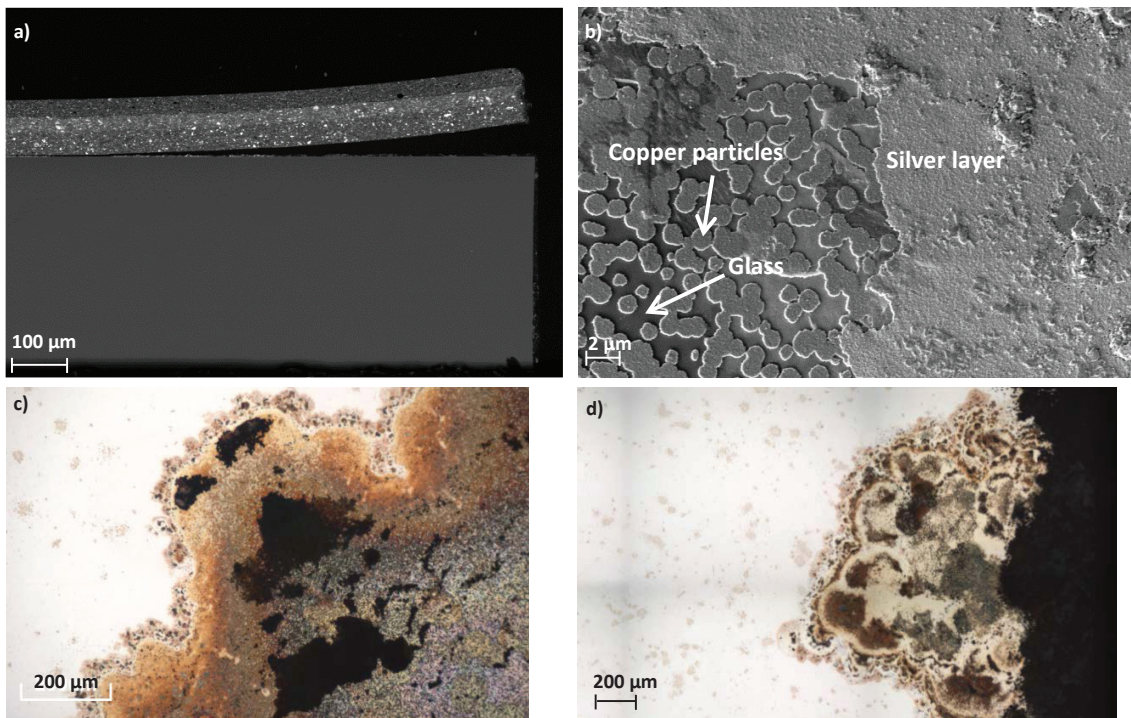

Fig. 8: a) Cross section of edge corrosion of sample 'C 1' after 2000 hours of Damp Heat testing; b) Top view of glass surface after delamination of paint layers in corroded area close to edge; c and d) light microscopic view of edge corrosion

An overview of the different appearance of degradation types under accelerated aging testing is shown in Fig. 9. The evolution of the spots has been monitored over time, showing small growth rated for certain spots.

Fig. 9: Degradation effects in different accelerated aging tests

The detected pitting corrosion spots outdoors of 'C 2' samples were best reproduced in the CASS test. Fig. 10 shows a SEM cross section analysis after 480 hours of CASS testing (compare to Fig. 5). Only two pitting corrosion

spots were found on the two samples tested. The size of the pitting corrosion spots was measured with the light microscope to be 840 and 300 µm. Thus, 480 hours of CASS testing does not seem to be enough to reproduce the 3 years outdoor exposure as spot sizes and spot density are smaller than in outdoor exposure. Fig 10 shows a glass splint close to the center of the corrosion spot. The glass splint seems to be a manufacturing defect (it is coated with silver from the top, see Fig 10 b) and might be the starting point of the localized corrosion spot. On the other hand, a sample preparation artefact is unlikely but cannot be completely excluded.
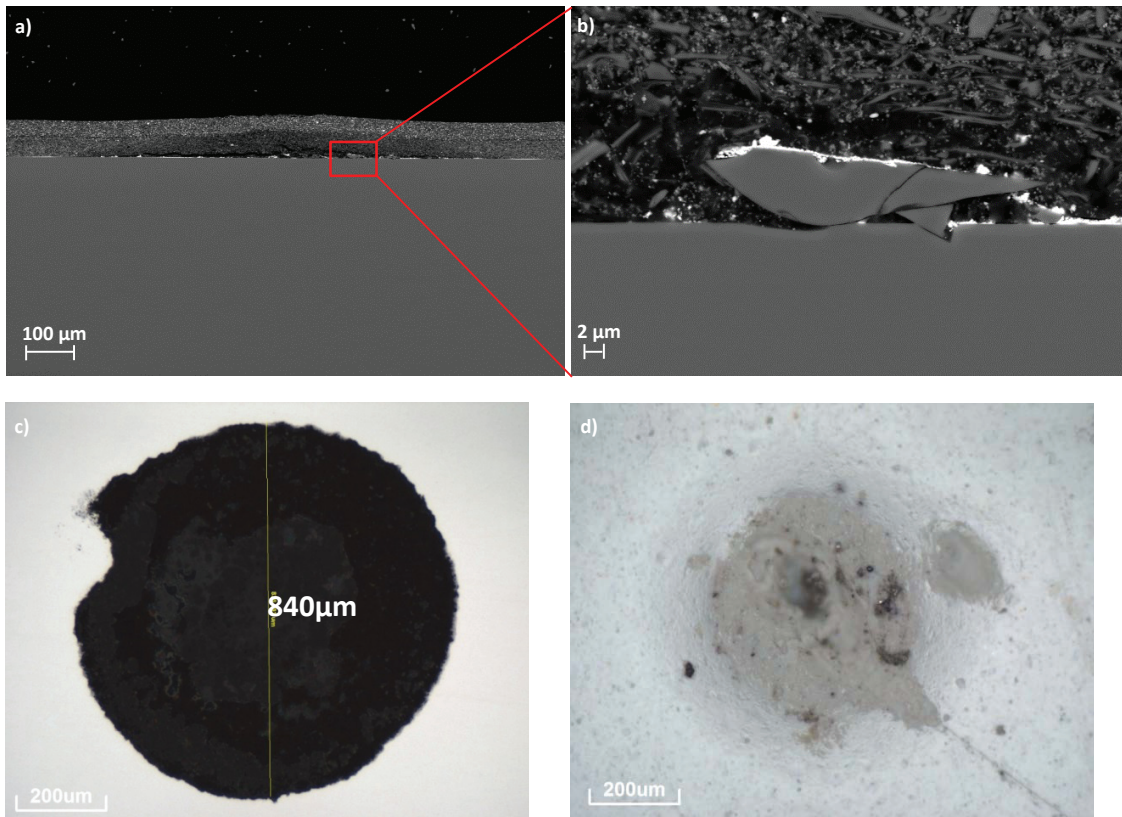

Fig. 10: a) Cross section of corrosion spot of 'C 2' sample after 480 hours of CASS testing; b) glass splint in the glass-silver interface; c) light microscopic view of corrosion spot from glass side; d) corresponding pinhole in top paint layer viewed in the light microscope.

5. Conclusions

Accelerated aging testing of samples that showed degradation outdoors and of samples that are outdoor-proven is a good method of checking the effectiveness of the accelerated test methods. From the performed analysis with three outdoor-proven mirrors and two materials that degraded outdoors none of the carried out accelerated aging tests was capable to point out differences among the materials. In fact, the samples that degraded outdoors showed excellent performance under accelerated aging conditions showing almost no pitting corrosion spots. It can be concluded that the NSS, CASS, UV+Humidity and Damp Heat test are not suited to make life time estimations of the tested mirror materials in this study. From those tests, the most appropriate seems the CASS, as it reproduced similar pitting corrosion spots as observed outdoors in Australia. The testing time of 480 hours is not sufficient to simulate 3 years of exposure.

The analysis of pitting and edge corrosion effects of outdoor exposed samples showed the presence of chlorides and sulfates within the corroded area. Thus, testing of additional accelerated aging tests which simulate aggressive industrial environments is regarded important. At the outdoor exposed samples, pinholes in the top coating have been found which were associated to pitting corrosion spots of the silver.

Specular reflectance measurements as a performance indicator of the mirror quality during accelerated testing is problematic because of severe glass corrosion at elevated testing times. Glass corrosion reduces specularity significantly and it has not been observed during outdoor exposure. As a consequence, glass corrosion should be suppressed in accelerated testing, for example by protecting the glass front side with sealing films.

Acknowledgements

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