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Influence of microstructure on temperature-induced ageing mechanisms of different solar absorber coatings

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ABSTRACT

Ageing mechanisms at high temperatures were investigated for various commercially available solar thermal absorber coatings. The absorber surfaces were sputtered chromium–chromium oxide based coatings on copper, aluminium and anodized aluminium substrates, an evaporated titanium oxy-nitride coating on copper substrate and an electroplated black chromium coating on nickel coated copper. The absorbers were aged at high temperature according to ISO standard draft EN 12975-3-1 at 278 °C for 600 h. The ageing mechanisms and degradation of the absorbers were analyzed by optical measurements (solar absorptance by UV/vis/NIR spectrophotometer and thermal emittance by FTIR spectrophotometer), microstructural analysis was made by field-emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM) with EDS, and composition analyzed by time-of-flight elastic recoil detection analysis (TOF-ERDA) before and after the ageing tests. The ageing and degradation of the absorber coatings were observed. The ageing mechanisms were the diffusion of substrate atoms into the coating or all the way into the coating surface and the oxidation of the chromium or the titanium in the absorber coating. The microstructure of the absorber coatings affected stability at high temperatures. Absorbers with a dense sputtered coating structure aged significantly less than more porous structured coatings.

1. Introduction

Solar thermal collectors are an environmentally friendly and non-polluting way to gather energy. The reduction of greenhouse gasses is the main advantage of utilizing solar energy [1]. Solar thermal flat plate collectors are commonly used in Europe [2]. Until the 1990s, the most common absorber coatings in flat plate collectors were electroplated black chromium coatings. The electrochemical deposition process from hexavalent chromium produces toxic and carcinogenic liquid waste. However, production costs of black chromium are low; so it is still used in flat plate collectors [3–7]. As a result of the environmental issues, physical vapour deposited (PVD) absorber coatings have since been developed. Nowadays, magnetron sputtering is a widely used PVD deposition process for absorber coatings. Magnetron sputtering is suitable for the large area deposition of thin films and it has a relatively high deposition rate. This technique is used to deposit absorber coatings that produce less pollution than conventional electrochemical methods. In last few years, magnetron sputtered chromium/chromium oxide or chromium/chromium oxy-nitride coatings have increased their market share significantly [1,8–14].

The efficiency of the solar thermal collectors has been developed significantly and thus the operation and stagnation temperatures of absorber coatings have increased. Further development of the collectors and new solar applications like solar cooling and industrial solar heating are further raising absorber operating temperatures [15]. The first solar thermal collectors in the 1950s and 1960s had a relatively low stagnation temperature [1,16]. Since the first collectors, solar absorber coatings have been developed actively [8–11,17–22], and used in advanced collector designs with improved efficiency [23–25]. The enhancement of coatings processes and the introduction of the PVD coating methods have improved the optical properties of coatings. Nowadays, solar absorptance of the most common high-quality commercial absorbers is about 95% and the thermal emittance is 4–5%. Thanks to these innovations, the operating temperature and stagnation temperature have increased. The highly selective PVD coatings have suffered from the stronger loads (200–215 °C [26]) at stagnation. For conventional black chromium coatings stagnation temperature was 180–200 °C [26].

The ageing phenomena of absorber surfaces at high temperatures over 250 °C have been investigated in relatively few studies. Nevertheless, the diffusion of copper at high temperatures has

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been widely studied in microelectronic applications [27–34]. In microelectronics, copper has been found to diffuse easily into a silicon substrate and form a Cu_3Si compound at 200 °C and higher temperatures [35–37]. In black chromium solar absorbers, ageing at high temperatures has been reported to include the oxidation of metallic Cr [38], desorption of water from the coating during initial phase degradation [38] and diffusion of copper and nickel substrates [3]. Yin et al. [39] studied sputtered Cr/Cr_2O_3 cermet absorber coatings and found that optical properties were unchanged at 300–400 °C whereas at 500 °C solar absorptance decreased in one hour tests in vacuum. However, the ageing mechanisms were not discussed. Barshilia et al. [40] reported that a $Cr_xO_y/Cr/Cr_xO_y$ coating on copper was stable in air at 300 °C for 2 h or in longer 250 h tests at 250 °C, while at higher temperatures in air the coating degraded due to the oxidation of Cr crystallites, increased surface roughness and formation of CuO. There are, however, some high-temperature solutions for flat plate collectors. Barshilia et al. [41,42] heat treated $NbAlN/NbAlON/Si_3N_4$ and $TiAlN/TiAlON/Si_3N_4$ absorber coatings on copper substrate in air for 2 h up to 600 and 900 °C, respectively. The optical properties of the coatings were maintained without significant changes up to 500 °C and 625 °C. These coating structures are very complex and so far not commercially available. Stability for a short time period at a certain test temperature can be used to compare absorber samples to each other and reveal the ageing mechanisms in the absorbers but the accelerated ageing test according to the ISO standard draft [43] is related to real operating temperature and predicts service life-time. New investigations are in progress to develop accelerated ageing test procedures for solar thermal collectors in extreme climate conditions [44].

Degradation processes in solar absorbers have been said reported to be caused by high temperature, high humidity, condensation of water, and/or sulphur dioxide as an airborne pollutant [38]. In the case of humidity, corrosion mechanisms have been reported in absorber coatings on aluminium substrates [45]. Between 2007 and 2011, SPF tested nine absorbers on aluminium substrate, where four of them passed and five failed, and nine absorbers on copper substrate, where seven passed and two failed. Failures were also attributed to the condensation test. Therefore, moisture tests are of significant importance especially for aluminium substrates. Probably, some of the absorbers studied here degrade by moisture like in study [45]. Therefore, aluminium absorbers need more moisture research but the results of this study should be applied for temperature-related phenomena only. All of these processes influence overall degradation, and this should be taken into account when evaluating absorber durability. However, only high temperature exposure was studied here, the other ageing processes are beyond the scope of this work.

The aim of this study was to deepen the knowledge of the ageing mechanisms in common commercially available solar absorbers regarding future high-temperature applications, such as solar cooling and industrial process heat. For domestic hot water (DHW) and house heating applications, most of the absorbers studied have exceeded a 25-years lifetime according to the manufacturers. We investigated how these solar absorbers behave at prolonged high-temperature exposure. It is important to understand ageing phenomena as a basis for the further development of the absorber coatings to be used at higher operating temperatures. Therefore, we studied typical absorber coatings on widely used substrates.

2. Experimental

2.1. Studied solar absorbers

The absorber coatings under investigation were typical commercial absorbers, supplied by four manufacturers. The absorbers are presented in Table 1. Depending on the supplier, the deposition methods and coating materials were different. Absorbers 1 and 3 were 100 nm thick sputtered chromium/chromium oxy-nitride coatings on copper substrate. Absorbers 2 and 6 were similar coatings but on aluminium substrates. Absorber 4 was a 120-nm-thick chromium/chromium oxide coating on anodized aluminium. Absorber 5 was a 100-nm-thick evaporated titanium oxy-nitride coating on copper. Absorber 7 was a 200-nm-thick electroplated black chromium coating with a 3000-nm-thick nickel layer between the absorber coating and the substrate. All of the coatings had a modern graded structure from more metallic to dielectric towards the surface. The antireflection (AR) layers were tin oxide for absorbers 1–3 and silicon oxide for absorbers 4–6. Electroplated absorber 7 had a rough chromium oxide surface layer which is assumed to act as an antireflective layer. The substrates were copper, electroplated nickel-coated copper, aluminium and anodized aluminium plates.

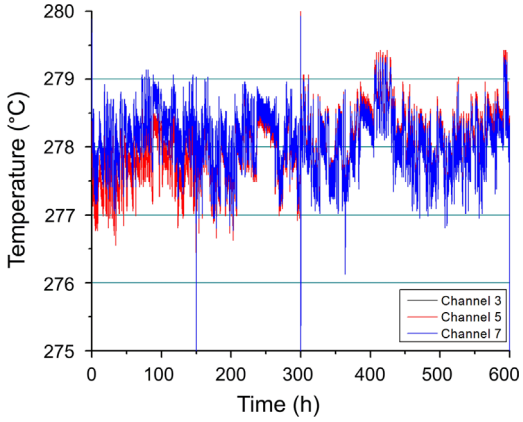

Fig. 1. Homogeneity of the temperature inside the Heraeus furnace at 278 °C, measured by three temperature sensors in different positions in the furnace. Temperature accuracy is about ± 1.5 °C. A furnace door was opened at 150 h and 300 h.

Table 1
Different absorber coatings investigated in this study.

	Substrate	Absorption layer	AR layer	Coating method
1	Cu 0.2 mm	Cr+O+N 100 nm	Sn+O 50 nm	Reactive sputtering
2	Al 0.4 mm	Cr+O+N 100 nm	Sn+O 50 nm	Reactive sputtering
3	Cu 0.12 mm	Cr+O+N 100 nm	Sn+O 50 nm	Reactive sputtering
4	Anodized Al 0.4 mm, anodized layer 140 nm	Cr+O 120 nm	Si+O 70 nm	Reactive sputtering
5	Cu 0.2 mm	Ti+O+N 100 nm	Si+O 100 nm	Reactive evaporating
6	Al 0.4 mm	Cr+O+N 100 nm	Si+O 80 nm	Reactive sputtering
7	Cu/Ni-layer 0.2 mm/3000 nm	Cr+O 200 nm	Rough Cr+O	Electroplating