Investigations of the interactions of CO₂, O₃ and UV light with silver surfaces by in situ IRRAS/QCM and ex situ TOF-SIMS

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1. Introduction

The interaction between a metal surface and its surrounding atmosphere with the subsequent formation of surface films formed by corrosion products affects many parts of infrastructure and electronics, but also works of art and cultural heritage. The most important factors which have an influence on the atmospheric corrosion processes are the relative humidity (RH), temperature, gaseous pollutants and particulates present in the ambient atmosphere [1,2]. Degradation and corrosion of metals involves very complex processes occurring at the gas–solid and liquid–solid interfaces. For metals exposed to ambient atmospheres, there are several interfaces where critical processes can occur. Despite that, most metals when exposed to ambient air are immediately covered with a thin film of oxide or oxyhydroxide. If the atmosphere contains water, meaning a certain relative humidity, hydroxyl groups are formed towards the atmospheric phase. Furthermore water will adsorb on this hydroxylated surface forming an adlayer where the amount of layers depends on the RH content of the surrounding atmosphere. Additionally, acidifying gases, such as CO₂, H₂S, SO₂, etc. can form solvated species or react with water or with other accommodated species in the water layer, and contribute to the degradation in a variety of chemical reactions [3–7]. The influence of acidifying gases such as SO₂ and H₂S on silver has been studied extensively, but the influence of CO₂ on a molecular level and the subsequent reactions with silver surfaces are still discussed in the literature [8–10].

Another aspect involved in atmospheric corrosion is the UV light induced photocorrosion. Crystalline materials such as silver absorb light and this energy can initiate chemical reactions which would otherwise not occur. Seemingly such effects influence the occurring corrosion mechanism during atmospheric exposure. Until now there is still a lack of knowledge concerning this photocorrosion of silver at a sub-μm level and the question is, if absorption of photons enhances the silver corrosion rate. Furthermore, the influence of strong oxidizing agents, such as ozone or hydrogen peroxide (H₂O₂) which might be present also in ambient atmosphere, has not been well documented yet [11–18]. Despite the potential importance of acidifying gases, UV light and oxidizing agents on atmospheric corrosion processes detailed experimental investigations on silver surfaces under controlled conditions are rare. For this reason the main aim of this study was to provide in situ chemical information of surface reactions of polycrystalline silver during exposure to different controlled atmospheres containing 50% and 90% RH, as well as CO₂, O₃, and to UV light. This in situ study has been performed by means of
three complementary analytical techniques namely a combined in situ IRRAS/QCM set-up and ex situ TOF-SIMS.

2. Materials and methods

2.1. Samples

The specimens are physical vapour deposited (PVD) silver-coated quartz crystals (99.99% purity) from Maxtek Inc. (USA, electrode material silver, diameter 2.54 cm, thickness 333 μm; AT-Cut) and stored in a desiccator until experimental deployment. This material is characterized by a homogeneous distribution of round silver particles (around 70 nm in diameter), thus creating a well-defined surface for the generation of reproducible data sets during the weathering experiments without any necessary sample pre-treatment.

2.2. Weathering and irradiation experiments

Weathering of the samples was carried out in an in situ IRRAS/QCM weathering cell [19]. The system for generating the moist air with CO2 and O3 is shown in Fig. 1. The air stream for the weathering process is generated by using dry synthetic air which is provided by a compressor (Jun-Air, Germany, Model OF301-4B 5) in combination with a pure air generator (Sigma-Aldrich, Austria, Nitrox Model 140). The quality of the pure air is achieved by using high efficiency pre- and post-desiccant filtration. The dry air stream is separated, where one part is humidified in a bottle containing distilled and deionized water and afterwards combined with the untreated airflow to the desired levels of relative humidity (RH). With this weathering system the humidified ambient atmosphere can be batched with 125–1000 ppm of CO2 with CO2 concentrations of 250 ppm, with and without irradiation of UV light or addition of 300 ppb O3, respectively. This flow rate leads to a mean residence time of the moist air in the weathering cell of approximately 2.3 s, as the inner volume of the in situ cell is approximately 25 cm³. For the irradiation of the sample a UV lamp (Hönle UV Technology, Germany, Model 400 H/2) was used. This lamp has a spectral range from 200–580 nm with the main intensities at 250–350 nm and an intensity of illumination of 100 W cm⁻². The O3 was generated by an Ozonisator (Topchem GmbH, Germany, Model Airmaster OMX 500) and the O3 concentration in the gas stream was monitored by an ozone sensor (Aeroqual Limited, New Zealand, Model AQL S200, detection 0–0.5 ppm).

2.3. IRRAS – measurements

2.3.1. Instrumentation

The measurements were performed with the FTIR-Spectrometer VERTEX 80v of Bruker Optics. The source is an air cooled IR ceramic source; a KBr beamsplitter was used for a spectral range of 10,000–380 cm⁻¹; an aperture of 250 μm was chosen. The in situ cell described in Section 2.3.2, was placed in the sample compartment. IRRAS spectra were obtained by averaging 200 scans at a resolution of 4 cm⁻¹. The spectra were recorded as single channel spectra and afterwards converted to absorbance spectra (R/R₀), where R₀ is the single channel spectrum of the sample obtained after 15 min exposure to dry synthetic air before starting the weathering experiment (background); R is the single channel spectrum of the weathered sample.

2.3.2. In situ IRRAS measurements

The IRRAS/QCM cell (infrared reflection absorption spectroscopy/quartz crystal microbalance) for in situ investigations enables one to perform IRRAS and QCM measurements simultaneously [19]. It is made of acrylic glass with gas in- and outlets, two zinc-selenide windows and a polymethylmethacrylate (PMMA) window for the irradiation with UV light. In the centre of this unit is the sample holder with the integrated QCM sensor head. For the experiments the quartz crystals are placed from the back of the cell into its position which assures that the sample is not shifted out of its position during the measurements and that the sample surface is always in the focal point of the IR beam. Rotate- and tiltable uncoated gold mirrors are mounted on the base plate, and ensure an angle of incidence of the IR beam of 78° off normal to the sample surface [22]. The IR beam from the FTIR spectrometer is reflected by a plane uncoated gold mirror, passes through a perpendicular mounted ZnSe window and hits the sample surface under a grazing angle of incidence. The reflected beam leaves the chamber through the second ZnSe window and is then reflected by another plane uncoated gold mirror onto the optical system of the spectrometer with a mercury cadmium telluride (MCT) detector (cut-off frequency: 800 cm⁻¹) which allows sensitive detection of the IR radiation.

2.4. QCM – measurements

To obtain gravimetric information from the occurring surface reactions a quartz crystal microbalance (Maxtek Inc., USA, QCM) was integrated in the cell [19]. This is a mass-sensitive device detecting mass changes <0.4 ng cm⁻². Due to possible surface reactions occurring on the silver surface exposed to humidity and CO2 with and without exposure to UV light and O3 these mass changes are recorded in situ with the QCM. The used AT-cut quartz crystals have a resonance frequency of 5 MHz, which changes in proportion to a change in mass as described by the Sauerbrey equation [23]. The QCM sensor head is placed from the back into the cell, fixing the sample crystal in the sample holder [19].

2.5. TOF-SIMS – measurements

Ex situ secondary ion mass spectrometry was performed with a TOF-SIMS® (ION-TOF GmbH, Germany), equipped with a Bi⁺ LMIG (liquid metal ion gun) and operated at 25 keV. For depth profiling two ion beams operate in the dual beam mode. The first beam (Bi⁺) generates the secondary ions (100 μm × 100 μm), which are analysed in a time of flight mass analyser. During the flight time,
the second beam delivered by a Cs⁺ thermal ionization source erodes a crater on the sample surface, in this case 300 μm x 300 μm. For the Cs⁺ ions an energy of 0.25 keV was chosen to obtain improved depth resolution while probing the thin corrosion layer [24,25]. Additionally, Cs⁺ ions enhance the formation of negatively charged secondary ions (like CO₃²⁻ or AgO⁻ for example) by reducing their work function [28]. In all measurements, the incident ion dose is kept below the static limit of 1 x 10¹² ions/cm².

3. Results and discussion

The influence of UV light, O₃, CO₂ and relative humidity content on polycrystalline silver surfaces was investigated in situ by IRRAS and QCM measurements; furthermore ex situ TOF-SIMS measurements were accomplished. Table 1 gives an overview on the experiments presented.

3.1. In situ IRRAS results

3.1.1. Influence of UV light

The polycrystalline silver samples were weathered under 90% RH with addition of 250 ppm CO₂ and additionally irradiated with UV light for the first 30 min of the weathering experiments. After 30 min the UV light was turned off and the weathering process was continued with 90% RH and 250 ppm CO₂ for another 30 min, which results in a total exposure time of the samples of 60 min. The obtained time resolved IRRAS spectra (taken every 2 min) are shown in Fig. 2. There the growth of two main absorbance bands can be observed at 1221 and 1109 cm⁻¹ are shown in Fig. 2. There the growth of two main absorbance bands can be observed at 1221 and 1109 cm⁻¹ wavenumbers. Furthermore a small signal is visible at 1160 cm⁻¹ which becomes noticeable as a shoulder of the absorbance band at 1160 cm⁻¹. As known from literature [19–21,26] the band at 1221 cm⁻¹ corresponds to the CO₃²⁻ asymmetric stretching vibration, the band at 1109 cm⁻¹ to the –C–O asymmetric stretching vibration and the band at 1160 cm⁻¹ to Ag–OH vibrations. Therefore, the evolution of those three bands can be correlated to the formation of a basic silver carbonate species (AgOHAg₂CO₃) on the sample surface. The evolution of these absorbance bands already starts 6 min after weathering under 90% RH, 250 ppm CO₂ and UV light. During the first 30 min of weathering these two absorbance bands are constantly increasing with time. After turning off the UV light and continuing the weathering process with 90% RH and 250 ppm CO₂ only, an initial fast increase of the absorbance band at 1221 cm⁻¹ can be observed. This is followed by a constant decrease until the end of the weathering period. Contrary, the band at 1109 cm⁻¹ is constantly increasing until the end of weathering experiment. The increase of the band at 1109 cm⁻¹ is seemingly caused at the expense of the band at 1221 cm⁻¹ which corresponds to the CO₃²⁻ vibration. As it is known that Ag₂CO₃ is not very stable in water [3], it can be supposed that the formed Ag₂CO₃ surface species is subsequently dissolved in the present surface water film leading to a decreasing CO₃²⁻ signal.

3.1.2. Influence of ozone

To investigate the influence of O₃ on these surface reactions compared to UV light polycrystalline silver samples were exposed to an atmosphere containing 90% RH, 250 ppm CO₂ and 300 ppb O₃ for 30 min. After 30 min of weathering the O₃ was turned off and the weathering process was continued with 90% RH and 250 ppm CO₂ only. The obtained time resolved IRRAS spectra, which were taken every 2 min during the weathering process, are shown in Fig. 3. During the first 30 min of weathering, where O₃ was added to the atmosphere, only a doubled absorbance band at 1050 cm⁻¹ wavenumbers could be observed, caused by gaseous O₃ [27]. Contrary to the experiment with UV light irradiation of the surface no additional signals at 1221 and 1109 cm⁻¹ could be monitored. Also after 30 min of weathering and turning off O₃ no absorbance bands could be detected in the range of 1400–900 cm⁻¹ for another 15 min. Afterwards a slow evolution of the two bands at 1221 and 1109 cm⁻¹ could be observed. These two bands could already be identified on the sample exposed to humidity, CO₂ and UV light and in fact are assigned to the CO₃²⁻ and –C–O asymmetric stretching vibration. Obviously during addition of O₃ to the weathering stream no basic silver carbonate-like species can be formed on the sample surfaces.

3.1.3. Comparison of the influence of CO₂, UV light and ozone

Fig. 4 summarizes the IRRAS results of the samples exposed to CO₂, UV light and O₃ at 90% RH. Each graph shows three spectra obtained after 30 min (Fig. 4a) and 60 min (Fig. 4b) of weathering with addition of 250 ppm CO₂ only, with CO₂ and UV light, and CO₂

Table 1

Overview of the performed experiments indicating the different weathering conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total exposure time 60 min</th>
<th>Results</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1st 30 min</td>
<td>2nd 30 min</td>
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<tr>
<td>1</td>
<td>90% RH 250 ppm CO₂</td>
<td>UV light</td>
</tr>
<tr>
<td>2</td>
<td>90% RH 250 ppm CO₂ 300 ppb O₃</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>90% RH 250 ppm CO₂</td>
<td>UV light</td>
</tr>
<tr>
<td>4</td>
<td>50% RH 250 ppm CO₂</td>
<td>UV light</td>
</tr>
<tr>
<td>5</td>
<td>50% RH 250 ppm CO₂ 300 ppb O₃</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50% RH 250 ppm CO₂</td>
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and O₃, all at 90% RH content. After 30 min of weathering no growth of absorbance bands could be observed for the sample only weathered with 90% RH and 250 ppm CO₂. Upon irradiation with UV light two absorbance bands at 1221 and 1109 cm⁻¹ wave-numbers are clearly visible. During addition of O₃ no growth of any absorbance band could be observed, except the band caused by gaseous O₃ itself. After the first 30 min of weathering the UV light and the O₃ were turned off, meaning that all three samples were continued to be weathered with 90% RH and 250 ppm CO₂ for another 30 min. The IRRAS spectra obtained from the samples weathered under those conditions and taken after 60 min of total weathering time are shown in Fig. 4 b. For all three weathering conditions two absorbance bands at 1221 and 1109 cm⁻¹ wavenumbers are observable. The spectrum of the sample which was exposed to 90% RH and 250 ppm CO₂ only shows an equal growth of the two absorbance bands after 60 min of weathering. The sample irradiated with UV light for the first 30 min the absorbance band at 1221 cm⁻¹ is more prominent compared to that at 1109 cm⁻¹. After 60 min, meaning 30 min after turning off the UV light, the band at 1221 cm⁻¹ decreases while the band at 1109 cm⁻¹ increases. For the sample exposed to O₃ no absorbance bands were visible during O₃ exposure. After turning off O₃ for 30 min two absorbance bands are clearly visible.

Summarizing the results of Fig. 4 leads to the following conclusion. On a silver surface exposed to 90% RH and 250 ppm CO₂ the formation of small amounts of basic silver carbonate-like species on the sample surface between 30 and 60 min of weathering can be observed. Additional exposure to UV light results in a higher basic silver carbonate formation rate, but the formed Ag₂CO₃ species seemingly is only stable in the presence of UV light, as the signal at 1221 cm⁻¹ decreases constantly after turning off the irradiation source. This might be caused by a dissolution of this formed degradation product in the present surface water film. Contrary to these results the addition of O₃ to the CO₂ containing humidified weathering stream does not result in any basic silver carbonate formation on the sample surface as long as O₃ is added to the moist CO₂ stream. As soon as the O₃ stream is turned off basic silver carbonate is formed on the sample surface, also under these conditions. Analyzing these results leads to the conclusion that UV light directly enhances the formation of silver carbonate-like species on the sample surface, while the addition of O₃ induces a different surface mechanism. Seemingly only intermediates are formed in the presence of O₃ leading to no signals in the range of 1400–900 cm⁻¹. After the addition of O₃ to the CO₂ containing weathering stream is stopped these intermediates are able to form a basic silver carbonate species on the sample surface. Therefore the conclusion can be drawn that O₃ acts as an “activator” of the silver surface.

3.1.4. Influence of relative humidity
In order to accomplish the studies and investigate the influence of the RH, experiments were performed in atmospheres with 50% RH (Fig. 5). Again IRRAS spectra were taken after 30 min (Fig. 5a) and 60 min (Fig. 5b) of weathering. For the sample only exposed to 50% RH and 250 ppm CO₂ no absorbance bands occur after 30 and 60 min. The sample weathered with 50% RH, 250 ppm CO₂ and exposed to UV light shows a very small to negligible absorbance band at 1109 cm⁻¹ after 30 min, which is also visible after 60 min.

![Fig. 3.](image) In situ time resolved IRRAS spectra, 1300–1000 cm⁻¹ wavenumbers, taken every 2 min from polycrystalline silver surfaces exposed to 90% RH and 250 ppm CO₂ for 60 min. Additionally, 300 ppb O₃ was added to the atmosphere for the first 30 min of weathering.

![Fig. 4.](image) In situ IRRAS spectra of three polycrystalline silver samples exposed to 90% RH and 250 ppm CO₂ for 60 min. Additionally, one sample was irradiated with UV light the second specimen exposed to 300 ppb O₃ for the first 30 min of weathering. The third sample was neither exposed to UV light, nor to O₃. Spectra were taken after 30 min (a) and 60 min (b) of weathering.
Also the sample exposed to 50% RH, 250 ppm CO₂ and 300 ppb O₃ does not show any absorbance bands, besides gaseous O₃, neither after 30 min nor after 60 min of weathering. These experiments clearly show and prove the importance of the RH content of the surrounding atmosphere on atmospheric corrosion mechanisms.

3.2. In situ QCM results

For more detailed assessment of the surface reaction mechanisms QCM data were accomplished simultaneously to the IRRAS experiments, in order to observe the in situ mass change during the weathering process. The areas of the absorbance bands at 1221 and 1109 cm⁻¹ were calculated by integrating the obtained spectra every 10 min of weathering and correlated with the IRRAS results. The progression of those band areas was compared to the overall mass gain during the measurements (Fig. 6) to elucidate if the observed mass increase is caused by the species characterized by the signals at 1221 and 1109 cm⁻¹.

3.2.1. Influence of UV light

Fig. 6a shows the QCM and IRRAS results of the sample weathered in 90% RH, 250 ppm CO₂ and irradiated with UV light during the first 60 min of weathering. The QCM results show that during the first 30 min of weathering, where the atmosphere contained 90% RH and 250 ppm CO₂ under UV light exposure, there is a constant mass increase, reaching a final mass of 0.35 µg cm⁻² after 30 min of weathering. Upon turning off the UV light and continuing the weathering a significant increase from 0.35 to 0.6 µg cm⁻² can be observed. This mass is nearly constant for 10 min (40 min of total weathering time) and then slowly starts to decrease reaching a mass of 0.4 µg after 60 min. Correlating now these mass changes to the simultaneously obtained IRRAS absorbance band areas, given by the dots in Fig. 6a, shows a strong dependence of the mass changes to the absorbance band areas indicating the growth of silver carbonate-like species on the sample surface. This perfect correlation of the data obtained from IRRAS and QCM is a further strong hint that the dominating degradation product is a basic silver carbonate species.

3.2.2. Influence of ozone

Fig. 6b shows the QCM and IRRAS results for the sample weathered in 90% RH, 250 ppm CO₂ and 300 ppb O₃. In O₃ containing atmospheres (the first 30 min of weathering) a fast mass increase until a final mass of 0.6 µg cm⁻² can be observed. After 30 min the O₃ was turned off and the weathering process in the humidified CO₂ stream continued leading to a further – but more slowly progressing – mass increase until reaching a final mass of 0.7 µg cm⁻² after 60 min of weathering. Comparing this mass progression to the calculated band areas of the IRRAS measurements clearly shows that the overall mass gain obtained from the QCM measurements has to be caused by additional surface reactions.
The observation of this significant mass increase in O₃ containing atmospheres and the results obtained by IRRAS spectra that no basic silver carbonate species is formed under such conditions may lead to the following assumption: Through addition of O₃ (a strong oxidizer) a film of Ag₂O is formed on the silver surface causing this fast mass increase detected by QCM. The formation of Ag₂O could not be detected by IRRAS as the bands are found between 800 and 300 cm⁻¹ wavenumbers. Unfortunately, these wavenumbers are outside the detection range of the detector available for our studies. To clarify this suspicion and to further verify the results of the in situ IRRAS/QCM measurements ex situ TOF-SIMS was performed.

3.3. Ex situ TOF-SIMS results

Fig. 7 shows the CO₃²⁻, AgO⁻ and OH⁻ signals obtained from the samples weathered for 60 min in 90% RH and 250 ppm CO₂ once irradiated for the first 30 min with UV light (Fig. 7a), the other time exposed to 300 ppb O₃ for the first 30 min (Fig. 7b). With these TOF-SIMS measurements depth profiles of the weathered sample surfaces could be obtained. The time scale (40 s) corresponds to a depth of approximately 20 nm. This was calculated by using the average sputter rate at an acceleration energy of 0.25 keV.

Fig. 7a shows, that on the surface of a silver sample weathered under the above described conditions, Ag₂CO₃ and AgOH are formed, but nearly no Ag₂O. The fast decrease of the CO₃²⁻ and OH⁻ signal shows that only a minor amount of these corrosion products was formed on the surface. Contrary to these results Fig. 7b displays that the highest signal is caused by OH⁻, followed by CO₃²⁻ for the outermost surface layer. As soon as the signals of CO₃²⁻ and OH⁻ decrease the AgO⁻ caused signal increases. This suggests that underneath a thin layer of mainly Ag₂CO₃ and AgOH an additional surface adlayer of Ag₂O must have been formed. Comparing the surface species formed on the sample exposed to UV light and the specimen exposed to O₃, it can be stated that on both samples an Ag₂CO₃ species was produced, even though more Ag₂O could be found on the surface exposed to UV light. The AgOH species is mainly found on the sample exposed to O₃, but it is also present on the sample, which was exposed to UV light. Finally the Ag₂O species, which is hardly present on the UV irradiated sample forms a more prominent layer on the sample exposed to O₃. These results prove the prior assumption that a silver surface immediately forms Ag₂O species upon O₃ exposure. After turning off the O₃ the outermost layer of the formed Ag₂O layer instantly reacts with the ambient atmosphere (90% RH and 250 ppm CO₂), which leads to the formation of a combined AgOHAg₂CO₃ surface species.

4. Conclusions

The initial interaction of relative humidity, CO₂, O₃ and UV light with polycrystalline silver surfaces has been followed by simultaneous in situ IRRAS/QCM measurements. During the exposure of silver to synthetic air with 90% RH, 250 ppm CO₂ and either addition of 300 ppb O₃ or irradiation with UV light the formation of a basic silver carbonate surface species could be followed time resolved for the first 60 min of weathering. It also could be shown that exposure of the silver surface to UV light or the presence of O₃ in the weathering stream enhances the formation rate of the corrosion products formed (AgOHAg₂CO₃ species) even though in different ways. While UV light directly enhances the formation rate of AgOHAg₂CO₃, O₃ seemingly prior forms a Ag₂O species, which subsequently reacts after turning off O₃ to form AgOHAg₂CO₃. Additionally, the crucial importance of the amount of relative humidity content during these reactions could be demonstrated. The performed ex situ TOF-SIMS measurements could proof the presence of three corrosion products on the weathered surfaces, namely Ag₂CO₃, Ag₂O and AgOH. However, the 3-dimensional distribution of these corrosion products depends on the weathering conditions chosen for the experiments. The results presented here reflect the significance of environmental influences such as relative humidity content, presence of CO₂ and O₃ as well as UV light radiation on the corrosion rate and the corrosion products formed on silver surfaces.

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