Quantified In Situ Analysis of Initial Atmospheric Corrosion

Surface heterogeneity, galvanic effects and corrosion product distribution on zinc, brass, and Galvalume

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Abstract

The interaction of the surface of a pure metal or an alloy with the surrounding atmosphere occurs in a highly complex interfacial regime. During atmospheric corrosion this interfacial regime involves the metal surface, often covered by a naturally formed oxide layer of a few nanometers thickness; an aqueous adlayer, typically with a thickness of a few to a few tens of nanometers, and the atmosphere from which airborne particles, oxygen, and gaseous pollutants dissolve into the adlayer and influence the atmospheric corrosion process.

This thesis work is mainly concerned with the initial atmospheric corrosion of zinc and brass induced by carboxylic acids (120 parts per billion of formic, acetic, or propionic acid) in laboratory air with 90% relative humidity. This model system has been chosen to mimic indoor corrosion with carboxylic acids as major corrosion stimulators. The study forms part of a broader research program with the ultimate goal to provide a computer model of the early stages of atmospheric corrosion of copper, zinc and copper-zinc alloys, induced by carboxylic acids. Particular emphasis has been given to identify and quantify the corrosion products formed and to determine their lateral distribution over the corroding surface. This has been accomplished through a multi-analytical approach in which two main techniques are infrared reflection absorption spectroscopy (IRAS) which can identify and quantify corrosion products with a relative accuracy of about 10%, and confocal Raman microspectroscopy (CRM) which can identify and resolve corrosion products with a surface lateral resolution of better than one micrometer.

The corrosion products identified on pure zinc are zinc oxide (ZnO) and various forms of Zn-carboxylates. On brass, the main corrosion products identified are a cuprite (Cu₂O)-like phase and various forms of Zn-carboxylates. For pure zinc and brass the formation rates of corrosion products in presence of the investigated acids depend, among others, on their deposition velocity and acid strength. The interaction of pure zinc and brass with humidified air containing carboxylic acids follows two spatially separated main pathways: a proton-induced dissolution of metal ions followed by the formation of oxides,
and a carboxylate-induced dissolution followed by the deposition of metal carboxylates.

When applying this multi-analytical approach, it has been possible to distinguish between anodically and cathodically active areas for brass, but not for pure zinc. Galvanic effects have been shown to play a significant role during the initial corrosion of brass.

Further evidence of the selective formation of corrosion products has been found when exploring the more complex heterogeneous surface of Galvalume, a commercial aluminum-zinc alloy coating. This material has been exposed to humidified laboratory air with additions of carbon dioxide (CO₂) and sodium chloride (NaCl) and to a marine atmospheric environment. Initiated in the interdendritic zinc-rich areas, a uniform aluminum oxide (Al₂O₃) layer is formed. This oxide exhibits an inhibiting effect on the subsequent formation of other corrosion products, including aluminum oxyhydroxide (AlOOH), aluminum hydroxide (Al(OH)₃), ZnO, zinc hydroxycarbonate and zinc hydroxychloride.
List of papers

This thesis is based on the following papers, referred to in the text by their Roman numerals I-V:

I. Initial oxidation of zinc induced by humidified air: a quantified in situ study
   Qiu, P.; Persson, D.; Leygraf, C.
   Journal of the Electrochemical Society (2009), 156(3), C81-C86

II. Initial atmospheric corrosion of zinc induced by carboxylic acids: a quantitative in situ study
    Qiu, P.; Persson, D.; Leygraf, C.
    Journal of the Electrochemical Society (2009), 156(12), C441-C447

III. Initial oxidation of brass induced by humidified air
     Qiu, P.; Leygraf, C.
     Applied Surface Science
     Submitted

IV. Multi-analysis of initial atmospheric corrosion of brass induced by carboxylic acids
    Qiu, P.; Leygraf, C.

V. Evolution of corrosion products and metal release from Galvalume coatings on steel during short and long-term atmospheric exposures
   Qiu, P.; Leygraf, C.; Odnevall Wallinder, I.
   Materials Chemistry and Physics
   Submitted
Contribution to the papers

Besides the respondent, being the main author of the listed papers and having performed the major part of the experimental work, the following persons have contributed to the papers:

I. D. Persson, Swerea KIMAB, helped with the optical calculations part. AFM measurements were performed by F. Zhang and J. Pan.

II. D. Persson, Swerea KIMAB, helped with the optical calculations. R. Robinson, Institute of Surface Chemistry, helped with SEM measurements.

III. SKPFM measurements were carried out by F. Zhang and E. Bettini. M. Sababi helped with metallographic analysis.

IV. SKPFM measurements were performed by F. Zhang and E. Bettini. XPS analysis was carried out by I. Odnevall Wallinder.

V. SEM imaging was performed by O. Karlsson, Swerea KIMAB. XPS analysis was carried out by I. Odnevall Wallinder. G. Herting and D. Lindström provided metal runoff part analysis.
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1 Introduction

1.1 Atmospheric corrosion

Atmospheric corrosion as a science has a history of almost one hundred years, starting with W. H. J. Vernon’s pioneer work on sulfur dioxide (SO₂) and carbon dioxide (CO₂) induced metal corrosion. Atmospheric corrosion is the result of interaction between a material: mostly a metal, stone, glass or polymer, and its surrounding atmospheric environment. While durability of structural materials is not affected until corrosion is extensive, minor corrosion may be of great importance for monuments and architectural ornaments, and may cause failures in electronic devices.

To reduce economic losses caused by corrosion, the suitability of different materials and of protective coatings have been investigated using different methods. Field exposures in various atmospheres, determining the mass loss, are used for evaluating corrosion kinetics. Characterization of corrosion patina formed under natural conditions, but also systematic laboratory studies, are commonly used for evaluating the corrosion mechanisms. The characterization of corrosion products becomes important in studying atmospheric corrosion. The development of the subject is thus relying on the development of analytical techniques.

Practical metal surfaces typically used for atmospheric corrosion studies are heterogeneous, due to compositional variations and surface defects, and may result in differences in nobility along the surface. These differences, resulting in separate anodic and cathodic areas, will influence metal dissolution and the formation of species on the metal surface, in the same manner as in galvanic corrosion.

1.1.1 Corrosion stimulators

The most important indoor and outdoor corrosion stimulators are water/humidity and air pollutants. The ambient relative humidity is crucial for initializing atmospheric corrosion. Once a metal surface is exposed to moist air, it will adsorb water
forming an aqueous adlayer, frequently resulting in a hydroxylated surface. The thickness of this aqueous layer depends on the relative humidity and surface properties, and is typically a few to a few tens of nanometers (nm) at room temperature.\cite{24} This aqueous layer constitutes the electrolyte, dissolving and dissociating gases and forming the environment for chemical and electrochemical reactions.\cite{25-26}

Besides gaseous pollutants, such as SO$_2$, ammonia (NH$_3$), and formic acid (HCOOH), aerosols and particles containing chlorides (Cl$^-$), nitrates (NO$_3^-$), sulfates (SO$_4^{2-}$) etc. are potential corrosion stimulators suspended in the gas phase.

The important corrosion stimulators for outdoor conditions are SO$_2$ and Cl$^-$. These substances may be of man-made or natural origin and their concentrations show large variations between environments. As an example, around five times higher SO$_2$ levels have been found at an urban site, as compared to a marine site, while the Cl$^-$ deposition rate may be fifty to one thousand times lower.\cite{27-31}

Figure 1.1. Reaction sequences for sheltered exposure of zinc in industrial or urban (SO$_2$/SO$_4^{2-}$) and in marine (Cl$^-$) environments respectively. Results are cited from Odnevall’s paper.\cite{32}

The composition of the atmosphere has a profound influence on the atmospheric corrosion of the material, which can be illustrated for two of the materials investigated herein, pure zinc and Galvalume, a commercial aluminum-zinc alloy coating intended for corrosion protection of steel. Figure 1.1 illustrates corrosion product formation sequences observed for zinc during sheltered exposure in atmospheres with either SO$_2$ or Cl$^-$ as dominating corrosion stimulators.\cite{18, 32} Corrosion products of similar composition as those
formed on sheltered zinc panels have been found also on Galvalume, in addition to Al(OH)$_3$, Al$_2$(OH)$_6$-H$_2$O and aluminum zinc sulfate hydrate.$^{[33]}$

Laboratory studies of CO$_2$ induced atmospheric corrosion of Galvalume have shown that the corrosion products are aluminum hydroxide, Al(OH)$_3$,$^{[34-35]}$ also including basic zinc aluminum carbonate (Z$_{n_6}$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O).$^{[36]}$

For indoor conditions, volatile organic acids such as formic acid (HCOOH), acetic acid (CH$_3$COOH), and less frequently studied, propionic acid (CH$_3$CH$_2$COOH) may have a significant influence on indoor corrosivity. This is illustrated by large amounts of carboxylates being formed on zinc and other metals after exposure in indoor environments with organic acids in concentrations of typically about 20 ppb.$^{[37-44]}$

Carboxylic acids in the atmosphere may exist as anthropogenic and/or biogenic air pollution, from automotive exhaust, biomass combustion for domestic and industrial heating, vegetation, organic coatings or emanating from the oceans. Other sources may be photochemical oxidation of organic species in air or water.$^{[45-46]}$

Carboxylic acids are the main corrosion stimulators studied in this thesis work. Knowledge of physical and chemical properties of these acids is thus of great importance to the work.

At a temperature of 298K, the acidity constant, or the (logarithmic) dissociation constant, is 3.77 for formic acid, 4.76 for acetic acid, and 4.87 for propionic acid.$^{[47]}$ The acidity or acid strength of an acid deposited on a metal surface will influence the corrosion behavior. Besides the acid strength, the deposition velocity, defined as the ratio between the deposition rate of each acid and its concentration in the gas phase, limits the gas supply to the aqueous adlayer, affecting the formation of corrosion products. It has been observed that the deposition velocity of these acids is highly dependent on properties of the metal surface although the detailed reason behind this is out of the scope of this work. As an example, on a pure zinc surface the acid deposition velocity is about five times higher than on a pure copper surface.$^{[16, 48]}$

Corrosive effects of organic acids on metal surfaces have been investigated under highly accelerated conditions, such as around 100% relative humidity (RH) and ppm levels of carboxylic acids. Corrosion rates obtained under such conditions were found to be highest in acetic acid, and to decrease in the order: acetic acid > formic acid > propionic acid.$^{[49-51]}$ Under less accelerated
conditions, in humidified air and 120 ppb carboxylic acid, the resulting corrosion rates were in the order formic acid > acetic acid > propionic acid. Both the acid concentration and the humidity thus have an influence on the corrosion process. Other types of studies have also shown the importance of the relative humidity. High initial adsorption rates observed by in situ vibrational sum frequency spectroscopy have been reported in both dry and humid air, but growth of a corrosion product layer was only evident in humid air.\cite{17, 52} Furthermore, the relative humidity level of the air can influence the growth rate of the corrosion product layer.\cite{38, 53} Only acids that are dissociated, a process requiring water, are corrosive. Electrochemical studies of metals in organic solvents containing different amounts of water indicate that water plays a significant role on the corrosion behavior of formic acid.\cite{54-55}

How the carboxylate groups coordinate with the substrate metal atom have also been studied widely. In general, the carboxylate group generate two different stretch bands in the infrared spectrum, the anti-symmetric stretch band, $\nu_a(\text{COO}^-)$, and the symmetric stretch band, $\nu_s(\text{COO}^-)$. The type of coordination to the divalent metal is determined by the separation between these two bands, designated $\Delta \nu_{a-s}$, through the following order: $\Delta \nu_{a-s}$ (unidentate) > $\Delta \nu_{a-s}$ (ionic) > $\Delta \nu_{a-s}$ (bridging) > $\Delta \nu_{a-s}$ (bidentate).\cite{56-63} Information of these features may be applied to determine the structure of the carboxylate group adsorbed to the surface metal atom.

1.1.2 The multi-regime of atmospheric corrosion

Atmospheric corrosion is a complex process of electrochemical nature, involving gas-liquid and liquid-solid interfaces.\cite{21, 64-66} With developments of analytical techniques the understanding of corrosion mechanisms has expanded from considering only the metal surface, to covering the complete interfacial regime involved. Figure 1.2 illustrates the condition of a metal surface exposed to ambient air, including three phases: air, possibly with gaseous pollutants, an aqueous adlayer and a metal substrate, and two interfaces between the phases.
1. Introduction

In the multi-regime, two interfaces: gas-liquid and liquid-solid are involved. The dominating electrochemical reactions within these interfaces are metal oxidation (anodic reaction) and oxygen reduction (cathodic reaction):

\[
M \rightarrow M^{n+} + ne^- \quad [1.1]
\]
\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad [1.2]
\]

GILDES modeling has been used for formulating a multi-regime model, which includes the major corrosion processes involved during initial atmospheric corrosion in the interfacial regime.\textsuperscript{[16, 48, 67-68]} Initialized by, e.g., carboxylic acids, SO\textsubscript{2} and nitrogen dioxide (NO\textsubscript{2}), dissociation occurs in the aqueous phase that results in the formation of protons (A\textsuperscript{+}) and ligand ions (B\textsuperscript{-}), which trigger metal ion dissolution as illustrated in figure 1.2. The first pathway includes dissolution of metal ions through interaction of protons with surface hydroxyl groups resulting in the formation of an oxide (MO). The second pathway includes dissolution of metal ions through interaction of the ligand with surface hydroxyl groups and precipitation of a metal complex (MB).
1.2 Motivation

This thesis work forms part of a broader study to obtain a molecular view of atmospheric corrosion, ultimately to be used for computer modeling of the atmospheric corrosion of Cu, Zn and Cu-Zn alloys induced by formic, acetic or propionic acid. These systems act as model systems to mimic indoor atmospheric corrosion and possibly capture the most important electrochemical, chemical and physical processes involved. Previous related papers have been concerned with the role of the interfaces involved,[53, 69] the surface-mediated dissolution process at the corroding surface,[70] and the identification and quantification of corrosion products on Cu.[16, 71]

The experimental approach used herein is based on a combination of spectroscopy (e.g., infrared reflection absorption spectroscopy, confocal Raman microspectroscopy), microscopy (e.g., atomic force microscopy), and other (e.g., quartz crystal microbalance) in situ techniques.

Significantly new information has primarily been gained in this doctoral study regarding the quantification, kinetics and lateral surface distribution of corrosion products formed on zinc and brass. In what follows the most important results will be presented and discussed topic by topic (chapters 4 to 10). They will be preceded by a theory section in which two important aspects of this doctoral study are discussed in some detail (chapter 2) and one experimental section (chapter 3), in which the experimental procedures and techniques are briefly described.
2 Theory

2.1 Vibrational spectroscopy

Infrared and Raman spectroscopy are the main techniques used herein to obtain vibrational spectra. When infrared or visible light impinges on a molecule, the interaction of the photon with the molecule can yield three different phenomena: absorption, scattering, or emission. Here we will focus on the first two, illustrated in figure 2.1, for the infrared and Raman processes.

![Diagram of IR absorbance and Raman scattering processes](image)

The illustration is cited from Johnson’s doctoral thesis.\cite{72}

Infrared absorption takes place if the photon energy corresponds to the difference between two stationary energy levels of the molecule. In infrared spectroscopy, the position of an absorption band is thus related to the absolute frequency of the incoming photon.

Raman scattering takes place as an “immediate” effect of interaction of the photon and the molecule when the photon energy does not correspond to the difference between any two stationary energy levels of the molecule. An incident photon with much higher energy than the vibrational transition excites
the molecule to a transitory virtual state. A new, inelastically scattered photon is created from the decay of this virtual state. This photon has energy different from that of the incident photon. Hence, the band position in Raman spectroscopy is associated with the difference in frequency between the exciting and the scattered photon.

Table 2.1. Selection rules of vibrational transitions in infrared and Raman spectroscopy

<table>
<thead>
<tr>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The energy of the photon matches the energy difference of vibrational levels: ( h\nu = \Delta E\nu )</td>
<td>1. The energy difference of the incident and scattered photon matches the energy difference of vibrational levels: ( h\nu_{0} - E\nu = \Delta E\nu )</td>
</tr>
<tr>
<td>2. The dipole moment changes during vibration: ( \frac{\partial \mu}{\partial Q} \neq 0 )</td>
<td>2. There is a change in polarizability during vibration: ( \frac{\partial \alpha}{\partial Q} \neq 0 )</td>
</tr>
</tbody>
</table>

\( \mu \) represents the dipole moment, \( Q \) is the normal coordinates.

\( \alpha \) represents the polarizability, \( Q \) is the normal coordinates.

The main selection rules, the conditions necessary for the vibration of the molecule to appear in the form of a vibration band, differ for the two kinds of spectroscopy. The selection rules are listed in table 2.1. They can also be used to determine the orientation of adsorbed molecules relative to the surface, based on the dipole moment when changing direction versus the electric field.

In the following a detailed description of the quantification of infrared spectra is given, since it is the major quantification method used in this work.

Beer-Lambert’s law describes the intensity of the infrared transmission spectroscopy.

\[
T = \frac{I}{I_0} = e^{-\rho l}
\] [2.1]
2. Theory

Where $I$ is the intensity of the transmitted light from a medium and $I_0$ is the intensity of the transmitted light from a reference medium. $\rho$ (cm$^{-1}$) is the absorption coefficient and $l$ (cm) is the thickness of the sample.

When the intensity is expressed as absorbance, the equation can be written as:

$$A = \log \frac{I}{I_0} = -\frac{\rho l}{\ln 10} \quad [2.2]$$

The absorption coefficient, $\rho$, describes the absorption of electromagnetic waves and can be expressed in several ways. For example, $\rho$ can be expressed in terms of the imaginary part of the refractive index, $\kappa$, and the wavenumber (cm$^{-1}$), $\nu$:

$$\rho = 4\pi\kappa\nu \quad [2.3]$$

The $\kappa$ can be obtained from transmission measurements at normal incidence. The imaginary part, $\kappa$, and real part, $n$, are related to each other through the Kramers-Kronig transformation $[76]$:

$$n(\nu_i) - n(\infty) = \frac{2}{\pi} P \int_{0}^{\infty} \frac{v k(v)}{v^2 - \nu_i^2} dv \quad [2.4]$$

$$k(\nu_i) = -\frac{2\nu_i}{\pi} P \int_{0}^{\infty} \frac{v v(v) - n(\infty)}{v^2 - \nu_i^2} dv \quad [2.5]$$

Therefore, calculations of $n$ and $k$ from transmission measurements result in optical data which can be used for calculation of IRAS spectra.

This is the main idea behind the quantification method used in this thesis work, as mainly presented in paper I and II.

The quantification calculations from IRAS spectra can be based on a model system, as illustrated in figure 2.2. A four layer system is used as an example, including air, water, oxide, and metal surface.

In this model, several approximations are made; the air and the metal surface are regarded as semi-infinite media with several plane parallel layers.
representing the surface films on the substrate. Each layer has a thickness and a complex refractive index as described above in equation [2.4] to [2.5].

![Four-layer model with optical indexes](image)

**Figure 2.2.** The four-layer model with optical indexes for calculations of *in situ* IRAS spectra.

The combined effects of reflectivity and transmittivity of all the layers is integrated in a stack matrix, which relates the electromagnetic fields in the incident medium and the final medium. Fresnel's equation is used for calculation of the reflectivity and transmittivity coefficients in the interface matrix. The stack matrix for a system of four layers is written as:

\[
S = I_{12}L_2I_{23}L_3I_{34}L_4
\]  

\[2.6\]

\(I\) is an interface transition matrix for incident beam reflection and transmission at each interface in the multilayer system, which relates the electric field on either side of the interface. \(L\) represents the incident beam propagation in each layer, which relates the electric fields within the layer.

Once the stack matrix is determined, the reflectance and transmission of the system can then be obtained from the elements of the stack matrix:

\[
R_{14} = \left| \frac{S_{14}}{S_{44}} \right|
\]  

\[2.7\]

\[
T_{14} = \frac{n_4 \cos \theta_4}{n_1 \cos \theta_1} \left( \frac{1}{S_{44}} \right)^2
\]  

\[2.8\]
Input data for the calculations are the complex refractive index as a function of the wavenumbers for each medium, the thickness of each layer, and the angle of incident beam. The estimated $n$, $k$, which derive from equation [2.3], [2.4], and [2.5] are then applied as starting values in the equation of [2.8] to compare with transmission experimental results from reference spectra until an acceptable agreement is obtained between them.

For further IRAS spectra quantification, e.g. to obtain layer thickness, the correct $n$ and $k$ value from above are then applied to equation [2.7] by adjusting each layer thickness in the calculations until an agreement between simulated spectra and experimental IRAS spectra is achieved. The resulting thickness of each layer is subsequently transformed to mass using the known density of each medium. It should be mentioned that the calculated IRAS spectra are based on optical data from bulk substances and that the optical properties of the thin surface film could deviate from the bulk substances.

In this study, programs written in MATLAB have been used for the calculations.

### 2.2 Galvanic corrosion

Galvanic corrosion, or bimetallic corrosion, will occur if two dissimilar metals are in electrical contact with each other and exposed to an electrolyte. A consequence of galvanic corrosion is an increased corrosion rate of the less noble metal because the cathodic reaction can take place more easily on the more noble metal than on the less noble one.\[^{79}\] Galvanic corrosion should be distinguished from selective corrosion, in which two or more components of the metallic material corrode at different rates. In corrosion science and for the development of corrosion protection, galvanic corrosion has been a substantially investigated subject.\[^{80-84}\] Galvanic corrosion has been theoretically investigated and basically expressed as:\[^{85}\]

$$I_g = \frac{(E_c - E_a)}{(R_a + R_c + R_s + R_m)} \quad [2.9]$$

$I_g$ is the galvanic current between the anode and the cathode, $E_c$ and $E_a$ are the open circuit potentials of the cathode and anode, $R_c$ and $R_a$ are the cathode
resistance and anode resistance respectively, $R_s$ is the resistance of the solution between the anode and cathode, $R_m$ is the metal resistance from the anode surface to the cathode surface. Normally $R_m$ is very small and can be neglected if the two electrode metals are in a direct electrical contact. Any factor that can affect these parameters will influence the galvanic corrosion, as summarized by Zhang for the Zn/steel system,\cite{86} in table 2.2.

Table 2.2 Possible factors that influence galvanic corrosion.\cite{86}

| a. | Reversible electrode potentials. |
| b. | Reactions, such as Zn dissolution, O₂ reduction, and H₂ evolution. |
| c. | Metallurgical factors, such as alloying, heat treatment, and mechanical working. |
| d. | Geometric factors, such as area ratio, distance, location, and shape and orientation. |
| e. | Electrolyte properties, such as ionic species, pH, conductivity, temperature, volume, flow rate. |
| f. | Surface condition, such as surface treatment, passive film, and corrosion products. |

The polarity and direction of galvanic current flow between two connected bare metals can be determined from the thermodynamic potentials of the metals. The metal which has the lower potential of the two is the anode in the galvanic couple, see table 2.3. for examples of standard electrode potentials.

Table 2.3 Standard electrode potential, measured at standard conditions.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Standard electrode potential, $V_{SHE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Al³⁺ + 3e→Al</td>
<td>-1.67</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn²⁺ + 2e→Zn</td>
<td>-0.762</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe²⁺ + 2e→Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu²⁺ +2e→Cu</td>
<td>+0.345</td>
</tr>
</tbody>
</table>
In reality, however, owing to the formation of an oxide or a salt film on the surface, the electrode potential can differ from the standard electrode potential. Aluminum is usually anodic to zinc in urban and marine atmospheres, indicating galvanic protection of zinc from aluminum.\cite{87} In other environments, like industrial marine condition, however, aluminum is cathodic to zinc.\cite{88}

Under atmospheric conditions, most metal surfaces will absorb water forming an aqueous adlayer, as introduced in chapter 1. Pollutants dissolved, ionic conductivity, volume and pH of the adlayer will significantly influence the result of galvanic action. These factors, even resulting in potential reversal, have been discussed in the literature. As an example, studies performed on the Zn/Fe couple in thin layer electrolytes emphasize the importance of solution resistivity (conductivity): the amount of galvanic corrosion of zinc generally increases with decreasing solution resistivity.\cite{22,89}

Table 2.4. Average corrosion rate for wires from wire-on-bolt testing for one year (1976-1977) at Swedish exposure sites.\cite{87}

<table>
<thead>
<tr>
<th>Couple (wire/bolt*)</th>
<th>Urban (Stockholm Vanadis) (mm/yr)</th>
<th>Rural (Ryda) (mm/yr)</th>
<th>Marine (Bohus-Malmön) (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/nylon</td>
<td>0.5</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Zn/Cu</td>
<td>2.2</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Zn/Al</td>
<td>0.4</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Zn/mild steel</td>
<td>3.0</td>
<td>3.3</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*Description of wire/bolt: A wire specimen of the metal to be tested is wound in the threads of a bolt or the other metal in the couple, while ensuring good electrical contact between the two members of the couple. Corrosion rate is estimated by determining the mass loss of the wire specimen.

While potentials and galvanic current of the coupled metals can be measured in solutions, investigations of galvanic corrosion in atmospheric environments are generally evaluated by weight-loss measurements. Table 2.4 shows the weight loss of zinc coupled to three different metals in different environments. Among the couples, zinc in the Zn/mild steel couple suffered the most severe
corrosion resulting from the galvanic action, so galvanic protection of mild steel from zinc should be the most efficient.

Weight-loss measurements mainly provide information on kinetics of galvanic corrosion, i.e. the propagation phase. To deepen the understanding of the galvanic corrosion mechanism, this work is concerned with the initial phase of galvanic corrosion. One of the main tasks of the work is to apply surface sensitive multi-analytical techniques to characterize the initial galvanic corrosion phenomena of brass and Galvalume coating under atmospheric conditions.
3 Experimental

This part of the thesis will give experimental details on zinc, brass, and Galvalume samples for laboratory and field exposures, also on the exposure conditions and analytical techniques used.

3.1 Sample preparation

3.1.1 Laboratory exposed samples

Four types of materials: zinc sheet, zinc-coated quartz crystals, brass sheet, and Galvalume coatings were selected for studying initial atmospheric corrosion, induced by humidified air and carboxylic acids, CO₂, or NaCl in synthetic laboratory air.

Zinc (99.7% purity), and brass (Cu-Zn, with 20% Zn by weight) samples were cut in 20 × 20 × 1 mm coupons. The coupons were abraded with SiC paper and polished with 0.25 μm diamond paste until an even mirror-like surface was obtained.

Zinc coated quartz crystals have been used for quartz crystal microbalance (QCM) measurements. A zinc film with thickness of around 1µm was sputtered onto the crystal with a Leybold sputtering setup with a zinc target (99.9%). During the deposition process, an Ar gas flow of 53 cm³/min was maintained by a mass flow meter. The total pressure was kept at 1.5×10⁻³ Pa during the coating process. A sputtering power of 340 W was used on the target. The substrate holder was rotated to obtain a homogeneous coating. After the coating process the zinc-coated quartz crystal was polished with 0.25 μm diamond paste.

Galvalume coatings, 20 μm thick, (55 Al-43.4 Zn-1.6 Si, wt %) applied on steel in a continuous hot-dip process were studied both in laboratory simulated conditions and field conditions. Samples (cut in 20 × 20 × 1 mm coupons) exposed in laboratory air were gently polished with 0.25 μm diamond paste.

To remove remaining diamond paste or grease, all samples were sonicated in ethanol, twice for around 5 minutes, and immediately flushed in dry nitrogen gas.
In order to reveal the grain boundaries of the brass surface, part of the polished brass samples were etched in a solution containing 2 M of hydrochloric acid (HCl) and 0.2 M of iron chloride (FeCl₃).

For the laboratory exposures, NaCl solution was deposited by the following procedure. Small quantities (20 µL) of a saturated solution of NaCl in 99.5% ethanol were distributed onto the Galvalume surface using a transfer pipette. The ethanol volatilized, whereby NaCl particles deposited on the Galvalume surface. The amount of NaCl deposited was around 15 µg/cm² determined gravimetrically.[90]

3.1.2 Field exposed samples

Samples for field exposures are commercial available pure zinc sheet (99.9 % purity) and Galvalume. Large panels (300 cm²) and small coupons (40 cm²) were exposed for runoff rate measurements and detailed surface analysis after different exposure periods. The materials were exposed single-sided in their as-received condition. To avoid any edge effects, cut edges were sealed with a polyurethane paint (without any corrosion inhibitor) aimed for corrosion protection. Furthermore, samples for metal runoff measurements were mounted on Plexiglas fixtures equipped with inclined gutters. Rainwater entered into the gutters was continuously collected and transported to polyethylene collecting vessels.

3.2 Exposure conditions

3.2.1 Laboratory exposures

The corrosive air used for laboratory exposures was generated by mixing three different air flows: dry air, humidified air, and air with one of the carboxylic acids or compressed CO₂ air.

The dry air was produced by passing compressed air through a Zander KEA 400 adsorption dryer equipped with particle and charcoal filters in order to dry and to reduce the CO₂ concentration. The concentration of CO₂ was around 20 ppm (ppm = volume parts per million) in the generated dry air. Humidified air
was produced by passing part of the compressed dry air to a humidifier, which contains water purified by a Millipore Rios-8 and Milli-Q PLUS purification system producing water with a resistivity of 18 MΩ/cm. The acid-containing air was prepared by passing dry air through permeation tubes (Vici Metronics) with the acid. By mixing two or three of the streams regulating the air flow rate, the desired humidified air or humidified acid-containing air or CO2-containing air was obtained. The corrosive air generator is schematically shown in figure 3.1.

![Figure 3.1. Schematics of corrosive air generator.](image)

The corrosive air flow is passed through the in situ exposure chamber. A cross-section of the chamber is shown in figure 3.2. The exposure chamber is made of stainless steel, inside covered with Teflon. The chamber is built to integrate IRAS and QCM for in situ measurements. So the chamber walls are equipped with CdTe windows for the infrared beam but keep corrosive air inside. A Teflon holder or a frequency counter for QCM is positioned at the bottom of the chamber. By doing this, the sample surface faces the incoming corrosive air.
Figure 3.2. Cross-section of IRAS and QCM integrated exposure chamber. Illustration is cited from Aastrup’s paper.[91]

Exposure conditions for the laboratory studies are 120±20 ppb carboxylic acid (acetic, formic or propionic acid), 350±20 ppm CO₂ air, 90±3% RH and 19.5±0.5 °C, and a laminar air flow along the sample surface of 3.5 cm/s. The flow rate is in the lower range of normal indoor air-flow conditions.[69]

3.2.2 Field exposures

Galvalume and zinc samples were exposed for 5 years (Dec 2004–Dec 2009) 5-10 m from the shoreline at the marine site Sainte Anne du Portzic, located on a cape outside the city of Brest at the north-west coast of France. The panels were freely exposed at an angle of 45° from the horizontal, facing south in accordance with the ISO 9226 standardized exposure condition for corrosion rate measurements.[92]

The site is characterized by low levels of gaseous pollutants, typically SO₂ < 2 μg/m³, NO₂ 7-22 μg/m³ and O₃ 40-80 μg/m³. The rain intensity is typically below 4 mm/hr. The corrosivity of the marine test site is classified as moderate (class C3 for pure zinc according to the ISO classification system 9223).[93-94]
3. Experimental

3.3 Analytical techniques

Multiple analytical techniques have been used in this thesis work, both in situ and ex situ.

The formation of corrosion products on zinc and brass during laboratory exposures has been monitored in situ by infrared reflection absorption spectroscopy (IRAS) and quartz crystal microbalance (QCM). After completion of laboratory and field exposures various analytical techniques have been used ex situ to characterize surfaces and corrosion products formed. Techniques used are cathodic reduction (CR), electrochemical impedance spectroscopy (EIS), confocal Raman microspectroscopy (CRM), grazing incident x-ray diffraction (GIXRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscope equipped with energy dispersive x-ray analysis (SEM/EDS), scanning Kelvin probe force microscopy (SKPFM) and optical calculations for the IRAS spectra and infrared transmission absorption spectra.

3.3.1 In situ techniques

Infrared reflection absorption spectroscopy (IRAS)

A Digilab FTS 4.0 Pro FTIR spectrometer was used for in situ IRAS measurements. A p-polarized infrared beam hits the sample surface at a grazing angle of around 78° from the surface normal, and is reflected to a nitrogen cooled mercury cadmium telluride (MCT) external detector by passing through the CdTe windows on the side wall of the exposure chamber, as described in figure 3.2. All spectra presented in this work were collected at a resolution of 4 cm⁻¹ through recording the average of 1024 scans.

Before each exposure, the sample was kept in either dry air or humidified air for 30 min to obtain the background spectrum. The sample was then exposed to corrosive air and the differential spectra were continuously recorded using the appropriate background spectrum. The IRAS spectra were recorded in absorbance units (-log (R/R₀)), where R is the reflectance of the exposed sample and R₀ the reflectance of the background. Subtracting the background spectrum
from the actual spectra eliminated peaks from physisorbed water and water in the gas phase within the absorption region of carboxylate.\textsuperscript{91} To obtain the growth kinetics of corrosion products, the relative height of each peak from the IRAS spectrum was plotted against exposure time and quantified according to the procedure presented in chapter 2.1. The same chapter also presents general selection rules for infrared spectroscopy.

**Quartz crystal microbalance (QCM)**

With QCM the correlation between mass and resonance frequency of a quartz crystal is used for sensitive mass measurements.

A QCM sensor probe (Maxtek MPS 550) with an AT-cut quartz crystal of 25.4 mm diameter was connected to a commercial frequency counter (Maxtek PM 740) and attached to the exposure chamber, as illustrated in figure 3.2. The resonance frequency was measured every 10 s and transformed to the corresponding mass through the Sauerbrey equation.\textsuperscript{95}

\[
\Delta f = -2f_0^2 (\Delta m)(\rho_q \nu_q)^{-0.5} \quad [3.1]
\]

\(\Delta f\) is the frequency shift, \(f_0\) the resonance frequency at the starting point of the exposure, \(\rho_q\) the density of quartz, 2.648 g/cm\(^3\), \(\nu_q\) the effective piezoelectrically stiffened shear modulus of quartz, equal to 2.947\times10^{11} g/cm/sec\(^2\), and \(\Delta m\) the mass change per unit area.

For a quartz crystal oscillating at a fundamental frequency of 5 MHz, the sensitivity is about 18 ng/cm\(^2\)/Hz, corresponding to approximately 2/3 of a monolayer of water.

**3.3.2 Ex situ techniques**

**Confocal Raman microspectroscopy (CRM)**

The CRM measurements were performed with a WITec alpha 300 system equipped with 532 nm laser source. A Nikon objective, Nikon NA0.9 NGC, was used for the measurements together with a pinhole with 100 \(\mu\)m diameter. Each Raman image was generated as follows. The Raman spectrum is obtained at each image pixel, resulting in the image consisting of stack Raman spectra. The
acquisition time for each Raman spectrum is in the order of 50 ms and the resulting stack Raman spectra are produced with a lateral resolution around 300 nm and a vertical resolution around 2 μm. When analyzing the selected peak lateral distribution, a corresponding Raman image can be generated by integrating its intensity in the stack Raman spectra using a WITec alpha software.

**Atomic force microscopy (AFM)**

AFM is a scanning probe microscopy based technique. It is designed based on atomic force theory with an AFM tip getting close enough to the material surface within the short range of atomic forces; the tip deflects back from the surface due to repulsive force interaction.\[^{96}\] By using a laser beam to detect this deflection, as well as a feed-back to regulate the distance between the sample surface and the tip, the surface topography of a sample can be generated. In general, two common scanning modes are used: contact mode (constant force or height)\[^{97}\] and tapping mode (non-contact).\[^{98}\]

The topography of the exposed sample surface has been investigated by an AFM from Quesant Instrument Ltd. The measurements were performed in contact mode with a commercially obtained SiN cantilever.

**Scanning Kelvin probe force microscopy (SKPFM)**

SKPFM is an AFM-based technique, which is used to acquire metal surface relative nobility and topography at the very same area simultaneously. The principle of SKPFM is to nullify the oscillating force caused by an electrostatic field between the conductive tip and the sample surface, by which the potential difference between the tip and the surface is determined. Surface features sized a few tenths of nanometers with less than 1 mV potential sensitivity can be qualitatively distinguished.\[^{99-101}\] This potential difference is named herein as Volta potential, with a physical meaning that is not completely understood. However, since it has been shown that the Volta potential measured in this way can be correlated to the corrosion potential,\[^{102-103}\] the Volta potential maps shown herein represent maps of relative nobility, i.e. indicating the tendency to corrode.

A Nanoscope IV with facilities for Volta potential measurements of the unexposed sample surface has been used. Volta potential data were collected
with the probe, antimony-doped Si supplied by Veeco, at a constant distance of 80 nm above the surface.

**Scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDS)**

SEM can be used to study the material surface or near surface structure. When equipped with EDS, it also has the capability of qualitative or quantitative analysis of the corresponding chemical composition with the possible lateral resolution of about 1 µm\(^2\).[104] This technique employs an electron beam to scatter radiation of the material within a defined depth, depending on the origin of the scattered electrons, in the order of micrometer.[105]

Three types of SEM/EDS instruments have been applied in this work for different purposes. A Philips XL 30 SEM/EDS instrument was used for morphology and elemental analysis of corroded zinc samples and or unexposed and etched brass samples.

A Hitachi TM-1000 table-top SEM with EDS facility was selected to obtain surface topography of corroded Galvalume coating samples.

The morphology of unexposed Galvalume coating surfaces was obtained by using a digital HKL Nordlys II F+ camera attached to an upgraded FEG-SEM Leo1530 (equivalent to Zeiss Supra 55). The software used was the Channel 5 suite from HKL. Elemental distribution was obtained by EDS mapping using a 50 mm\(^2\) X-Max SDD (Silicon Drift Detector) and the software INCA from Oxford Instrument.

**Electrochemical measurements**

To contribute to the identification of oxides on corroded pure zinc and brass surfaces, to deduce the average mass of oxides, and for measuring polarization resistance, cathodic reduction (CR) and electrochemical impedance spectroscopy (EIS) has been performed using a standard three-electrode cell with a Ag/AgCl electrode as reference and a platinum mesh as counter electrode. Exposed brass, copper and zinc coupons with 20 × 20 mm\(^2\) area acted as working electrodes. A 0.1 M sodium perchlorate (NaClO\(_4\)) solution was used as electrolyte. The electrolyte was purged with N\(_2\) for 30 min before starting each cathodic reduction and throughout its duration. A Solartron 1287
potentiostat was used for the CR measurements. The scan rate was 1.0 mV/s. The electrical charge corresponding to complete ZnO and Cu₂O reduction was obtained by integrating the current of each reduction peak using Corrview software. The equivalent mass of ZnO and Cu₂O was determined from Faraday’s law.\textsuperscript{[106]} Combining the potentiostat with a frequency response analyzer Solartron 1255, EIS was performed at the open circuit potential with a sinusoidal voltage signal of 10 mV applied over a frequency range of $10^4$-$10^2$ Hz.

**Grazing incident X-ray diffraction (GIXRD)**

XRD is based on diffraction of x-rays at various angles when a monochromatic x-ray beam irradiates a crystalline material, according to Bragg’s law.\textsuperscript{[107]} XRD provides information of the bulk of any material.\textsuperscript{[108]} In order to enhance the surface sensitivity, and collecting less bulk information, diffraction with x-rays at grazing angle incident on the surface can be an alternative.\textsuperscript{[109-111]}

GIXRD was carried out with a grazing angle of 88° versus the surface normal on a X’pert PRO PANALYTICAL system, equipped with an x-ray mirror (CuKα radiation) and a 0.27° parallel plate collimator on the diffracted side. The area of analysis was approximately $1 \times 1$ cm.

**X-ray photoelectron spectroscopy (XPS)**

The sample is irradiated by monochromatic x-rays at the same time a detector measures the kinetic energy and number of photo induced electrons from the material. The elemental information of the materials is determined by the detected kinetic energy.\textsuperscript{[112-113]} The corresponding relative amount depends on the number of electrons escaped. XPS is a surface sensitive technique, with an information depth of typically less than 10 nm.\textsuperscript{[114-115]}

XPS (Kratos AXIS HS system) measurements were performed on polished brass specimen as well as on the Galvalume coating before and after corrosion. Wide and detailed scans (pass energy 80 eV) of Cu 2p, Zn 2p, Zn LMM, Al 2p, Cl 2p, S 2p, C 1s and O 1s were accomplished with a monochromatic Al Kα x-ray source (1486.6 eV) operated at 300 W (15 kV/20 mA). The area of analysis was approximately 0.5 mm$^2$. Linear background subtraction and Gaussian peak deconvolution were performed for each photoelectron peak of interest.
**Atomic Absorption Spectroscopy (AAS)**

AAS can qualitative and quantitative determine chemical elements. The flame (thermal energy) can cause electrons of an atom to transit from ground state to an excited state by absorbing defined quantity of energy. In general, this amount of energy is specific to one element. The radiation flux with and without sample is measured and converted into concentration or mass by Beer-Lambert law. Depending on the sample concentration, graphite furnace is selected to measure sample for ppb range and flame for ppm range.

Total released concentrations of zinc and aluminum from field exposed zinc and Galvalume samples were determined by AAS (Perkin Elmer AAnalyst 800). Before measurements, collected runoff water from all the samples were acidified with 65% HNO₃ analytical grade to a pH less than 2. After acidification, the solutions were transferred for AAS measurements. Five replica readings were performed for each sample with the flame technique (AAS-F) and triplicate readings were performed during the graphite furnace (AAS-GF) analysis. Limits of detection were determined to 10 µg/L for zinc (AAS-F) and 20 µg/L for aluminum (AAS-GF). Quality control samples were analyzed every 10th sample for both methods to verify the calibration curves and to document the internal drift of the instrument.

**Infrared transmission-absorption spectroscopy**

This technique was used to obtain optical data for ZnO and Zn-carboxylates for the optical calculations. KBr pellets with ZnO and each Zn-carboxylate were prepared and used for obtaining transmission-absorption spectra using a Varian 7000 FTIR spectrometer averaging 1024 scans at a resolution of 4 cm⁻¹.
4 Quantification study of simulated indoor atmospheric corrosion of zinc (Paper I)

Methods for quantification of corrosion products are described in this part as well as their application for zinc exposed in humidified air (paper I).

IRAS spectra were recorded in situ for both zinc foil and zinc-coated quartz crystals exposed to 90% RH air after 72 hours, as illustrated in figure 4.1. This model system was studied aiming at simulating indoor corrosion of zinc. The peak at around 570 cm\(^{-1}\) is due to the formation of ZnO on the surface.

![Figure 4.1. In situ IRAS spectra of zinc foil and of zinc-coated quartz crystal in the region from 500 to 750 cm\(^{-1}\) after 72 h exposure in air at 90% RH. (Paper I)](image)

The mass change as measured with QCM is shown in figure 4.2. The sudden dips in the curve are from turning off and on the supply of humid air repeatedly during exposure. The repeated decrease and increase in humidity induced a sudden mass loss and mass gain respectively.

This mass change of around 1.5 µg/cm\(^2\) corresponds to the reversible desorption and adsorption of water.

The mass of corrosion product (ZnO) formed was estimated by multiplying the measured mass gain (from QCM) by 5.09 (equal to the molecular weight of ZnO divided by the atomic weight of oxygen).
Figure 4.2. Total mass gain vs. time for zinc exposed to air at 90% RH, as measured by QCM. (Paper I)

Figure 4.3. Cathodic reduction scans of zinc after different exposure periods in air at 90% RH. (Paper I)

The validity of this procedure was verified by cathodic reduction. Figure 4.3 shows cathodic reduction curves for zinc after different exposure periods. ZnO formation was derived from the reduction peak at -1.3 V$_{\text{Ag/AgCl}}$. The mass of ZnO is proportional to the electric charge according to Faraday’s law and was
calculated by integrating the current for the corresponding peak. The resulting ZnO mass after 72 h exposure is 27.5 µg/cm².  

IR based modeling was also used for quantitative results. A four-layer system was developed to quantify ZnO formed on the zinc surface in humidified air. Figure 4.4 shows the resulting simulated IRAS spectrum obtained from the four-layer optical calculations (figure 4.5) with an assumed ZnO thickness of 25.5 nm (Paper I).

Figure 4.4. Simulated IRAS spectrum based on the four-layer optical model calculations with assumed ZnO thickness of 25.5 nm. (Paper I)
Figure 4.5. The optical four-layer model with complex optical indexes, $\tilde{N}_1(\nu), \tilde{N}_2(\nu), \tilde{N}_3(\nu), \tilde{N}_4(\nu)$ for calculations of in situ IRAS spectra. $dw$ and $do$ represent the layer thicknesses of the aqueous adlayer and the ZnO layer respectively. (Paper I)

Figure 4.6 Relationship between the absorbance of the ZnO band at 570 cm$^{-1}$, measured by in situ IRAS, and corresponding ZnO mass obtained by QCM, cathodic reduction (CR), and optical calculations (OP). (Paper I)
4. Quantification study on zinc

Generally, the three independent quantification techniques exhibit good agreements, usually with a relative error of less than 10% as shown in figure 4.6. Moreover, they all turn out to be relevant methods for obtaining absolute masses of ZnO formed under current exposure conditions. However, with some deviation between each method: cathodic reduction slightly overestimates and the optical calculations slightly underestimate the ZnO amount comparing to QCM.
5 Kinetics of initial atmospheric corrosion induced by carboxylic acids (Paper II)

The quantification methods introduced in previous sections have also successfully been utilized to quantify corrosion products triggered by carboxylic acids in humid air on pure zinc.

Figure 5.1 shows in situ IRAS spectra collected after exposure of zinc to carboxylic acids air for 72 h. The main components identified are ZnO and various zinc carboxylates.

![In situ IRAS spectra of zinc after 72 h exposure in 120 ppb formic acid, acetic acid, or propionic acid. (Paper II)](image)

Figure 5.1 In situ IRAS spectra of zinc after 72 h exposure in 120 ppb formic acid, acetic acid, or propionic acid. (Paper II)
Figure 5.2 Mass of zinc carboxylate species and of ZnO as a function of exposure time based on the five-layer model calculations of in situ IRAS spectra obtained during exposure in formic acid, acetic acid and propionic acid. The lines between points are drawn for visual aid. (Paper II)

The quantitative data for each component formed has been obtained by using optical calculations based on a five layer model, which was introduced in section 2.1. Since the exact molecular formula of each zinc carboxylate was not possible to obtain, it was assumed that the optical constants of all possible zinc carboxylates formed under current exposure conditions could be represented by the optical properties of zinc carboxylate dihydrates, Zn(CHOO)₂·2H₂O,
5. Kinetics study on zinc

Zn(CH₃COO)₂·2H₂O, and Zn(C₂H₅COO)₂·2H₂O. The resulting absolute mass of each zinc carboxylate dihydrate and of ZnO formed in the three different carboxylic acid conditions have been plotted versus exposure time in figure 5.2. In all, the carboxylate formation rate increases in the order propionic acid < acetic acid < formic acid, whereas the zinc oxide formation rate exhibits the opposite trend: formic acid < acetic acid < propionic acid.

Based on the quantified IRAS-data the actual corrosion rate could be estimated by considering the total amount of Zn²⁺ in either ZnO or in zinc carboxylate. The corrosion rates obtained follow the order: propionic acid (0.22 µg/cm²/h) > acetic acid (0.07 µg/cm²/h) > formic acid (0.04 µg/cm²/h). These rates are about one order of magnitude higher than representative indoor field exposure rates.[38, 116] The difference is caused by the higher acid concentration (120 ppb), higher relative humidity (90%), and higher air flow rate compared to actual indoor conditions with typically 20 ppb of acid concentration, and an average relative humidity close to 50% in 0.1-1 m/s air flow rate.[117]

Not only the corrosion rate but also the deposition velocity of the acids into the aqueous adlayer could be estimated from the quantification data in figure 5.2. The deposition velocity increases in the order propionic acid (0.008 cm/s) < acetic acid (0.02 cm/s) < formic acid (0.08 cm/s). It turns out that the deposition velocity limits the acid supply into the aqueous adlayer which furthermore governs the zinc carboxylate formation. In all, the differences in deposition velocity and in acid strength between the investigated carboxylate acids largely govern the initial atmospheric corrosion of zinc induced by each acid.
6 Duplex oxide growth during exposure of brass to humidified air (Paper III)

So far, the corrosion mechanism of zinc induced by humidified air without and with carboxylic acids mixture has been studied with particular emphasis on corrosion product identification, quantification and growth kinetics. Because vast information is available for both pure zinc (this thesis work) and pure copper \cite{118}, an obvious continuation was to perform a similar study of a brass, i.e. a copper-zinc alloy, under similar exposure conditions. This chapter summarizes some results and highlights the growth and properties of the duplex oxide formed on brass in humidified air (Paper III).

Figure 6.1. In situ IRAS spectra in the region from 500 to 1000 cm\(^{-1}\) of brass, pure zinc and pure copper after 72 h exposure in synthetic air at 90% RH. (Paper III)

In situ IRAS spectra were continuously recorded during up to 72 h exposure of brass in synthetic air at 90% RH, see figure 6.1. Spectra of pure zinc and copper are included in the figure for comparison. The peaks at 660 and 570 cm\(^{-1}\) are from Cu\(_2\)O and ZnO respectively. The Cu\(_2\)O peak at 660 cm\(^{-1}\) for brass is slightly shifted to higher wavenumber and is broader as compared to the spectrum for pure copper.\cite{16} This indicates a compositional or structural change
induced by mixing ZnO into the Cu$_2$O layer and resulting in a more amorphous structure, which normally has a higher corrosion resistance.[64, 119]

The higher corrosion resistance for the altered Cu$_2$O-layer on brass was verified by EIS measurements, as shown in figure 6.2. It revealed that the corrosion resistance of the surface film was highest for brass and decreased in the order brass > copper > zinc.

![Bode plots of brass, zinc and copper in a 0.1M NaClO$_4$ solution, after exposure in humidified air at 90% RH for 72 h. (Paper III)](image)

The formation of a duplex oxide and the corrosion product quantity, as analysed by IRAS, was verified by cathodic reduction, with results shown in figure 6.3. The reduction peak around -0.62 V$_{\text{Ag/AgCl}}$ is most likely due to Cu$_2$O, whereas the reduction peak around -1.2 V$_{\text{Ag/AgCl}}$ is due to ZnO. The estimated mass of Cu$_2$O and of ZnO formed on brass is 0.7 and 0.6 µg/cm$^2$ respectively.
Figure 6.3. Cathodic reduction curve obtained in 0.1 M NaClO$_4$ solution for brass exposed to humidified air at 90% RH for 72 h. (Paper III)

In all, as evidenced by IRAS and electrochemical measurements, the duplex oxide layer formed on the brass surface under current exposure condition exhibits a more amorphous structure together with better corrosion resistance compared to the oxides formed on pure zinc and pure copper respectively. As expected, the corrosion mechanisms for the pure metals and the alloy may differ considerably in many respects. In what follows, the growth kinetics and lateral distribution of corrosion products on brass will be explored in some detail.
7 Galvanic effects observed during initial atmospheric corrosion of brass (Paper III and IV)

Within this stage it was not yet possible to separate anodic and cathodic processes on pure Cu and Zn using current analytical techniques based on spectroscopy and microscopy. When applying the same multi-analytical approach on brass exposed to humidified air it has, however, become possible to distinguish anodic and cathodic areas. It then became evident that galvanic effects play a role in the corrosion process of brass.

In this chapter we will summarize part of the results in paper III and paper IV from a galvanic corrosion point of view, in order to identify the anodically and cathodically formed reaction products triggered by humidified air with and without carboxylic acids, and based on the manifested unexposed heterogeneous brass surface.

7.1 Nobility variations along the surface of unexposed brass (Paper III)

The duplex oxide layer, identified on the brass surface after exposure in humidified air, indicates that galvanic corrosion takes place. Knowledge of the initial surface structure, prior to the exposure to corrosive conditions, thus is crucial for the understanding of the galvanic corrosion mechanisms. The Volta potential map shown in figure 7.1 clearly shows numerous darker rounded areas of lower Volta potential, i.e. lower nobility than the surrounding matrix. The size of lower nobility areas are comparable with some of the grains revealed on the etched brass surface, which may be grains with slightly higher zinc contents, see figure 7.2.
Figure 7.1. SKPFM Volta potential map of a diamond polished brass surface. Scan size 10 x 10 µm. The maximum Volta potential difference shown in the figure, from dark to light, is 80 mV. (Paper III)

Figure 7.2. SEM image displaying the microstructure of the etched surface of the same diamond polished brass sample as in figure 6.1. The arrow indicates an area with relatively high zinc content. (Paper III)
It is thus concluded that the surface of unexposed brass does indeed possess nobility variations, creating conditions for anodic and cathodic reactions during the early stage of atmospheric corrosion.

### 7.2 Kinetics of galvanic corrosion of brass in humidified air (Paper III)

Galvanic effects can affect corrosion rates. This is evident from figure 7.3, showing ZnO and Cu₂O growth kinetics, as derived from the in situ monitored IRAS spectra of figure 6.1. Based on the IRAS measurements, the masses of Cu₂O and ZnO after 72 h are estimated to 0.6 µg/cm² and 0.5 µg/cm² respectively. If considering the molar ratio of Cu and Zn in the alloy, the results clearly show higher ZnO growth as compared to Cu₂O growth. This is attributed to galvanic effects caused by the heterogenuous brass surface composition described in section 7.1.

![Graph showing absorbance of Cu₂O (660 cm⁻¹) and ZnO (570 cm⁻¹) versus exposure time for brass exposed to synthetic air at 90% RH. The error bars are based on triplicates.](image)

Figure 7.3. Absorbance of Cu₂O (660 cm⁻¹) and ZnO (570 cm⁻¹) versus exposure time for brass exposed to synthetic air at 90% RH. The error bars are based on triplicates. (Paper III)

It should be pointed out however, that the mass of this duplex oxide layer, 1.3 µg/cm², is much lower than the oxide layer formed on pure copper and on pure zinc under similar exposure conditions, with corresponding masses 8.4 µg/cm²
of Cu$_2$O and 27 $\mu$g/cm$^2$ of ZnO. A plausible explanation is the amorphous structure of the duplex layer formed, as indicated in chapter 6, which exhibits better corrosion resistance than the oxide films formed on zinc and on copper.

7.3 Kinetics of galvanic corrosion of brass in humidified air with carboxylic acids (Paper IV)

The galvanic effects found on brass, as a result from initial variations in surface nobility, were further investigated by introducing carboxylic acids into the humidified air.

Upon initial atmospheric corrosion of pure Cu or pure Zn induced by carboxylic acids, the corrosion products formed mainly consist of oxides (Cu$_2$O or ZnO) and various forms of Cu- or Zn-carboxylates. When a brass surface was exposed to similar conditions, only Cu$_2$O and various hydrated or hydroxylated Zn-carboxylates were formed. This was based on IRAS spectra and XRD patterns shown in figure 7.4 and figure 7.5 respectively.

![Figure 7.4 In situ IRAS spectra of brass after 72h exposure in humidified air with (a) formic acid, (b) acetic acid, and (c) propionic acid. (Paper IV)](image-url)
Figure 7.5. GIXRD patterns for brass after exposure for one month in humidified air with formic acid (a), acetic acid (b), and propionic acid (c). The peaks labeled as d, e, and f represents Cu(OH)$_2$·H$_2$O, Zn(HCO$_2$)$_2$·xH$_2$O, and Zn$_5$(OH)$_8$(CH$_3$CO$_2$)$_2$·xH$_2$O respectively. (Paper IV)

In order to further investigate the kinetics of initial galvanic corrosion, growth rates of Zn-carboxylate and Cu$_2$O on brass and on the corresponding pure metals have been compared. In the upper graph of figure 7.6, the $v_a$(COO-) absorbance and corresponding mass for brass and for zinc is shown versus exposure time. In the lower graph, the Cu$_2$O absorbance and corresponding mass for brass is compared to that for pure Cu. In both cases, the metals are exposed to humidified air with 120 ppb formic acid. The higher Zn-carboxylate growth rates on brass, compared to pure Zn, and the lower growth rate of Cu$_2$O on brass, compared to pure Cu, clearly show galvanic effects on the brass surface under the investigated exposure conditions.
Figure 7.6 Absorbance and corresponding mass of corrosion products as a function of exposure time: zinc carboxylate formed on brass and on zinc (top), Cu$_2$O formed on brass and on copper (bottom). Exposure conditions are humidified air with 120 ppb formic acid. Error bars are based on triplicate measurements. The lines between the points are for visual aid. (Paper IV).
8 Direct evidence of the formation of corrosion cells during initial atmospheric corrosion of brass (Paper IV)

The previous chapter summarized observed galvanic effects, as evidenced from the kinetics of corrosion product formation. These investigations have, however, not provided any direct visualization of anodic and cathodic areas. By studying brass as substrate and using the lateral resolution capability of CRM, it has become possible to analyze the distribution and role of anodic and cathodic areas.\[17, 52, 120\] This chapter will summarize part of the results in paper IV on how the lateral distribution of corrosion products and the galvanic cell sizes are influenced by carboxylic acids.

As concluded from IRAS measurements in chapter 7, the main corrosion products identified on brass after exposure in 120 ppb carboxylic acids are a Cu$_2$O-like oxide and Zn-carboxylate. Figure 8.1 shows Raman images obtained by integrating the $\nu_\text{a}(\text{COO})$ peak intensity from Zn-carboxylate in the range from 1550 to 1640 cm$^{-1}$ and the Cu$_2$O band from 600 to 680 cm$^{-1}$ in the stack Raman spectra. Pink-colored areas represent the distribution of carboxylate and green-colored areas represent Cu$_2$O. For all three acids, Zn-carboxylate was located in the centre and surrounded by Cu$_2$O. This observation is a solid proof of spatially separated anodic (Zn-carboxylate) and cathodic (Cu$_2$O) areas. Together with the observation of galvanic effects, it forms microscopic and spectroscopic evidence of the electrochemical nature of initial atmospheric corrosion.

A clear trend was seen for the centrally located Zn-carboxylate. Its size decreased in the order formic acid > acetic acid > propionic acid (figure 8.1. a-c). The size difference is believed to be due to differences in the ionic conductivity of the aqueous adlayer. From differences in acid deposition velocity and in dissociation constant for the carboxylic acids, the ionic conductivity decreases in the same order (highest for formic acid, lowest for propionic acid).\[48\]
Figure 8.1. Raman images of brass exposed one month to humidified air with formic acid (a), acetic acid (b), and propionic acid (c). The presence of Zn-carboxylate is represented by pink and of Cu$_2$O by green. Scan size 10 × 10 µm. (Paper IV)
9 Selective corrosion observed during atmospheric corrosion of more complex heterogeneous systems (Paper V)

Besides investigating galvanic effects on brass, another heterogeneous surface, a Galvalume coating (an aluminum-43.4% zinc coating on steel), has been investigated, although under different exposure conditions: humidified synthetic air and a natural marine environment, including CO₂ and Cl⁻ as the main pollutants. This part of the thesis mainly involves results from paper V.

![Surface morphology (a) and Volta potential image (b) of polished unexposed Galvalume surface. Arrow indicates zinc-rich area. Scan size 40 × 40 μm. (Paper V)](image)

Figure 9.1. Surface morphology (a) and Volta potential image (b) of polished unexposed Galvalume surface. Arrow indicates zinc-rich area. Scan size 40 × 40 μm. (Paper V)

Similar to what was observed on brass, the surface of the polished unexposed Galvalume exhibits nobility variations. These variations, which may produce spatially separated anodically and cathodically active areas, are due to compositional differences between interdendritic Zn-rich areas having a lower Volta potential, and dendritic Al-rich areas having a higher Volta potential, figure 9.1.

Upon exposure of Galvalume to humidified air the only corrosion product detected by in situ IRAS is Al₂O₃ (with a peak at 958 cm⁻¹), see figure 9.2.
Figure 9.2. In-situ IRAS spectra of pure zinc, pure aluminum and Galvalume surface exposed for 72h in 90% humidified air. (Paper V)

Figure 9.3. Intensity of zinc oxide and aluminum oxides as a function of the exposure time of polished pure zinc, pure aluminum, and Galvalume surface exposed in 90% humidified air. There is no substantial ZnO observed on Galvalume surface. (Paper V)

Figure 9.3 displays the absorbance versus time during exposure of pure zinc, pure aluminum and Galvalume in air with 90% relative humidity. A comparison of the absorbances (a measure of the absolute amounts) of the oxides detected reveals that Galvalume exhibits smaller growth rates of both Al₂O₃ and of ZnO
9. Selective corrosion observed on Galvalume

compared to the corresponding growth rate of the pure metals. This shows that
the formation rates are governed by kinetics rather than galvanic effects, due to
the formation of the highly protective Al2O3 layer on all parts of the surface.

The Raman image in figure 9.3 shows that Al2O3 is selectively formed in
zinc-rich areas. Corrosion of aluminum is thus more extensive in the zinc-rich
areas with lower Volta potential, showing effects of the differences in nobility
between zinc-rich and aluminum-rich areas.

![Raman image](image_url)

Figure 9.4. Raman image (scan size: 30×30 µm) of the Al-O-Si band
integrated between 923 and 1008 cm\(^{-1}\) for Galvalume after 72 h exposure in
humidified air. (Paper V)

The SEM-image and Raman-image in figure 9.5 of Galvalume after 1 year
marine site exposure reveal that the corrosion product formation selectively
occurs on the interdendritic areas, with some extent of dispersion evidenced in
Raman image. Together with other analytical information this suggests similar
composition of corrosion products after the marine field exposure and the
laboratory exposure with CO\(_2\)-containing humidified air and predeposited NaCl;
Al\(_2\)O\(_3\), AlOOH, Al(OH)\(_3\), ZnO, Hydrozincite, Simonkolleite, in addition to an
aluminum sulfate of unknown identity.
Figure 9.5. Corroded surface morphology (SEM image, a) and corrosion products lateral distribution (Raman image, b) for Galvalume after 1 year exposure at the marine site. The color combined Raman image represents Si (integrated between 470 and 550 cm\(^{-1}\), blue color), Si-O-Al (integrated between 923-1008 cm\(^{-1}\), yellow color), SO\(_4^{2-}\) (integrated between 970-1200 cm\(^{-1}\), red color), CO\(_3^{2-}\) (integrated between 1160-1480 cm\(^{-1}\), green color), and ZnO (integrated between 510-600 cm\(^{-1}\), white color).

The mass fraction (Zn/(Zn+Al)), demonstrated in figure 9.6 (a) which is obtained by XPS, shows the zinc-containing phases surface coverage reaches a maximum during the first year and then declined. The same trend of the average release rate of zinc is observed in figure 9.6 (b). This is due to the formation of the less soluble aluminum-rich phases on all parts of the Galvalume surface compared to zinc-rich phases.
9. Selective corrosion observed on Galvalume

Figure 9.6. The mass fraction, (a), \( \frac{Zn}{(Zn+Al)} \) and average release rates, (b), of zinc and aluminum for Galvalume exposed to non-sheltered conditions at the marine site of Brest, France, as a function of exposure time.

In all, variations in Volta potential of the unexposed Galvalume surface result in subsequent selective corrosion in the interdendritic areas, but in no accelerated formation rate of one phase at the expense of another at least under humidified air exposure condition. Hence, kinetics rather than galvanic effects are concluded.
10 Summary and outlook

The main emphasis of this doctoral study has been on the initial atmospheric corrosion of zinc, brass, and Galvalume induced by humidified air and carboxylic acids (zinc and brass) as well as by CO₂ and NaCl (Galvalume). Both in situ and ex situ analytical approaches have been applied to identify and quantify corrosion products formed, and to determine their lateral distribution over the sample surface.

Zinc corrosion products formed in humidified air with carboxylic acids have been successfully quantified by in situ IRAS integrated with QCM, showing good correlation with each other. Results obtained have further been compared with optical calculations and cathodic reduction, the former underestimating and the latter overestimating the amount of corrosion products formed comparing to QCM. The presence of carboxylic acids resulted in the formation of Zn-carboxylate at rates following the order formic acid > acetic acid > propionic acid, in consistency with the corresponding deposition velocity and acid strength, which are highest for formic acid and lowest for propionic acid.

Current available analytical techniques do not allow any direct microscopic or spectroscopic evidence of the anodic and cathodic processes on a zinc or a copper surface, although it is well known that atmospheric corrosion is of electrochemical nature. When applying the same multi-analytical approach on brass, and taking advantage of the lateral resolution capability of CRM, it has however been possible to distinguish anodic and cathodic areas from each other. By this multi-analytical approach it is evident that galvanic effects play a role for corrosion of brass exposed to humidified air with and without carboxylic acids. SKPFM results reveal nobility variations across the brass surface: Zn-enriched areas with lower Volta potential surrounded by areas of higher Volta potential.

For GILDES modeling of initial atmospheric corrosion, the observed galvanic effects will increase the understanding of the corrosion process. Taking acetic acid as example, the initial atmospheric corrosion may be described by a number of elementary steps. The first step is the dissociation of CH₃COOH upon entrance into the aqueous adlayer (step 1 in figure 10.1). Two pathways have been identified. The first includes proton induced dissolution of copper
followed by the formation of a Cu$_2$O-like layer (steps 2-5). These steps preferably occur on areas of the brass surface with higher Volta potential. The second pathway is acetate induced dissolution followed by Zn$_5$(OH)$_6$(CH$_3$CO$_2$)$_2$·xH$_2$O formation (steps 6-9). These steps preferably occur on areas with lower Volta potential, characterized by slightly higher Zn content.

Figure 10.1. Depiction of possible reaction pathways during initial atmospheric corrosion of brass induced by acetic acid in humid air. (Paper IV)

The electrochemical nature of atmospheric corrosion is evidenced through the galvanic effects, as proven by the kinetics of corrosion product formation: accelerated formation of Zn-carboxylate and retarded formation of the Cu$_2$O-like layer. Second evidence is the existence of spatially resolved corrosion cells: centrally located Zn-carboxylate surrounded by a Cu$_2$O-like layer.

The size of the Zn-carboxylate cells, decreasing in the order formic acid > acetic acid > propionic acid, is consistent with ionic conductivity properties of the acids in the aqueous adlayer.

Surface heterogeneity effects on initial atmospheric corrosion were seen also for the more complex surface of Galvalume. A similar multi-analytical approach was used as for brass. Galvalume is characterized by interdendritic Zn-rich areas, with lower Volta potential, and Al-rich areas, with higher Volta potential. After exposure in humidified air with CO$_2$ and NaCl as corrosion stimulators,
and also after marine field exposures, a selective corrosion was observed emanating primarily from the interdendritic areas, characterized by the lower Volta potential prior to exposure.

The main outcome of this thesis work is the combination of in situ and ex situ surface analytical techniques to qualitatively and quantitatively characterize corrosion products formed on pure zinc, brass, and Galvalume and further to distinguish anode and cathode areas from each other. By this outcome, the ultimate goal of this project was met, i.e. further elaborating the experimental basis for computational modeling of early stages of atmospheric corrosion on pure zinc, pure copper, and their alloys.

The heterogeneous brass surface creates a rather complex system for studying initial atmospheric corrosion. In this doctoral study it has not been possible to observe corrosion cells after shorter exposure times (i.e., of the order of days) by CRM, partly due to its inherently too high detection limit. Instead, by combining existing quantified data for zinc, copper and brass, it may be possible to elaborate a model system, in which zinc and copper form a bi-metallic couple. By adjusting the geometrical ratio between the metals in the couple it could be possible to mimic galvanic effects under real conditions, representing very early corrosion stages.

One of the most important observations in this work is that the size of the galvanic cells, formed on brass in the presence of carboxylic acid, is limited by the deposition velocity and dissociation constant of the acid. This effect was observed after about one month exposure. In situ CRM monitoring the evolution of corrosion cells may provide additional information on galvanic effects.

The corrosion behavior of the Zn-Cu system has been one of the main tasks of this study. Besides brass, another heterogeneous material, Galvalume, was explored. As for the Zn-Cu system, the quantification of corrosion products could be useful for further investigating properties of Galvalume and other alloy coatings, e.g. Galfan (a commercial 5% aluminum - 95% zinc alloy coating) utilizing the same techniques.
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