Filiform Corrosion of coated Aluminium Alloys

"a study of mechanisms"

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Filiform Corrosion of coated Aluminium Alloys

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1.1 Introduction
Aluminium and iron based alloys are often exposed to aggressive environments which contain water, oxygen, chloride ions, acid and many other impurities. These alloys are sensitive to corrosion even when they are protected with an organic coating. Rust spots on old cars are well-known examples.

Corrosion is defined as electrochemical degradation, occurring at the metal-solution interface where the metal is oxidised (anodic reaction) and species from the solution such as oxygen (cathodic reaction) are reduced. The rate of the corrosion reactions is reduced when the bare metal is isolated from the aggressive environment (i.e. an electrolyte solution), for example by applying an organic coating, or by the formation of an oxide layer. In the latter case the metal protects itself against further attack: the metal is passivated. Due to its passive behaviour, as a result of a well adherent and non porous oxide film, aluminium is a popular construction material.

Despite its good corrosion resistance, passive aluminium is attacked in certain environments, even when it is coated with an organic coating providing additional corrosion protection. In acid (pH less than 4) and alkaline (pH more than 8) solutions the oxide film on aluminium will dissolve and respectively $\text{Al}^{3+}$ ions and aluminate ions, $\text{AlO}_2^-$, are formed\(^1\). Local attack of the oxide layer is possible when the electrolyte solution contains chloride ions (pitting corrosion)\(^1\).

Filiform corrosion is a major point of concern when coated aluminium alloys are exposed to a humid atmosphere\(^2,3\). Most often filiform corrosion starts at defects in the coating such as cutting edges or local weak spots in the coating\(^2\). Filiform corrosion is initially a cosmetic type of attack but depending on the application area of the alloy, it may result in more serious damage to the construction. Filiform corrosion has been responsible for extensive damage, with extreme costs in various sectors of industry such as building, automotive and aircraft. In building industry it is nowadays a serious problem at facades and window frames\(^4\). When filiform corrosion is left unattended at aircraft's, the surface attack may develop into crevice corrosion around rivets\(^5\). This may result in serious damage to the
skin. Also stress corrosion cracking on high strength structural aluminium parts may initiate at corroded tracks left by filiform corrosion in critical areas of the aircraft.

This special type of localised corrosion is the subject of this thesis. Filiform corrosion is now reviewed briefly in section 1.2. The outline of this thesis is given in section 1.3.

1.2 Filiform corrosion
An example of filiform corrosion is shown in figure 1.1. The filament consists of two parts: the head and the tail. The corrosion reactions take place in the head which is filled with an electrolyte solution. The tail is filled with dry corrosion products. The boundary between the head and the tail is vague and therefore the nature of the corrosion products is slowly changing from gel-like near the head to dry further in the tail.

![Figure 1.1 A filament after 5 weeks exposure to 82% R.H. and 38 °C. Polyurethane coating on Al2024 T3 Clad alloy](image)

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Filiform corrosion is usually observed under organic coatings\textsuperscript{2,5,6,17}. It is observed on coated aluminium\textsuperscript{5,16}, magnesium\textsuperscript{5} and steel substrates\textsuperscript{5}. Filiform has not been developed on coated stainless steel substrates, or on monel, copper, brass, nickel, chromium, tin, lead, gold or titanium substrates\textsuperscript{5}. Filaments may also grow under the naturally present oxide layer on a metal substrate\textsuperscript{18-22} and under different pretreatment layers on (uncoated) substrates such as chromate, phosphate and anodised oxide layers, and under metallic coatings on steel substrates (tinplated, silver plated and gold plated steel), and aluminium (cladded aluminium alloys\textsuperscript{5} ). These examples suggest strongly that a layer, i.e. an organic coating, a metallic or pretreatment layer, is required for filiform corrosion to occur.

The practical conditions for filiform corrosion to occur are known reasonably well. In literature\textsuperscript{2,5,6-8,10} the following four conditions have been reported:

- an atmosphere of high relative humidity,
- permeability of the coating for water and oxygen,
- contamination at the coating-substrate interface with salts,
- the presence of defects in the coating.

Although the conditions are known, the exact mechanism of filiform corrosion is still subject of discussion.

1.3 Outline of this thesis
This thesis consists of six parts. In part II the mechanisms of filiform corrosion are discussed. In chapter 2 the general corrosion mechanisms of coated metal substrates are first reviewed. These mechanisms are anodic undermining (for coated aluminium substrates) and cathodic delamination (for coated steel substrates). The mechanism of filiform corrosion is also based on the mentioned mechanisms. This is discussed in detail in a literature review in chapter 3. From this review it becomes clear that for coated aluminium, the corrosion properties of the substrate are quite important for the filiform corrosion process. Therefore the passive film on aluminium, which is responsible for the good corrosion behaviour of aluminium alloys, is examined in part III. In chapter 4 impedance measurements have been performed to investigate the formation of a passive layer under potential control. The measurements can be explained with a model
based on the point defect model of Macdonald et al after considerable adjustment. Part IV concerns a study of the permeation properties of several coating systems. Capacitance measurements have been performed to monitor the water penetration. A new approach is proposed to analyse the capacitance measurements. In part V the results of filiform corrosion measurements are discussed. Finally the general conclusions are given in part VI.

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II CORROSION MECHANISMS

"A LITERATURE REVIEW"
Chapter 2

CORROSION MECHANISMS OF COATED METALS

General corrosion mechanisms of coated metal substrates, which are immersed in electrolyte solutions, are reviewed in this chapter. These mechanisms will also occur in case of filiform corrosion. After a brief discussion of corrosion of uncoated metals in section 2.2, the corrosion protection by organic coatings is reviewed. In section 2.3 mechanisms of coating failure will be evaluated, i.e. blister initiation and growth (section 1.3.1 and section 1.3.2), cathodic delamination and anodic undermining (section 1.3.3). The latter two are based on the differential aeration cell. Consequently, the oxygen transport for both mechanisms is discussed in section 1.3.4. The ionic charge transport between the anodic and cathodic sites in a blister is reviewed in section 1.3.5. Finally some conclusions are given.

2.1 General and local corrosion of metals

As mentioned in the previous section the anodic reaction is the dissolution of the metal. A number of cathodic reactions may occur depending on the conditions. In aerated neutral solution the main cathodic reaction is the reduction of oxygen (eq. 1.1). In acid solutions both hydrogen ions (eq. 2.2) and oxygen (eq. 2.3) are reduced while in neutral de-aerated solution water (eq. 2.4) is reduced. It should be noted that this reaction is very slow.

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  \hspace{1cm} (2.1)

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2.2)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm} (2.3)

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \hspace{1cm} (2.4)

General corrosion is described by the mixed potential theory which explains uniform corrosion attack (fig. 2.1a) by assuming an equal electrode potential for
the whole surface under stationary conditions\textsuperscript{1}. The reactions are normally shown in an Evans diagram as illustrated in figure 2.1\textsuperscript{b} for the diffusion controlled oxygen reduction reaction and a charge transfer controlled anodic reaction. The corrosion current $I_{\text{cor}}$, is defined as the current at the corrosion potential (mixed potential).

\begin{align*}
&\text{environment} \\
\text{Metal} &\quad \begin{aligned}
&O_2 \rightleftharpoons M^{2+} \\
&O_2 \rightleftharpoons M^{2+} \\
&O_2 \rightleftharpoons M^{2+}
\end{aligned}
\end{align*}

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{evans_diagram.png}
\caption{General corrosion of an uncoated metal in an electrolyte solution. The reduction of oxygen is diffusion controlled, yielding a cathodic limiting current. The anodic reaction ($M \rightarrow M^{2+} +ze^-$) is controlled by charge transfer. $I_{0,a}$ is the exchange current of the anodic reaction. An Evans diagram is shown in b).}
\end{figure}

Local corrosion may be the result of a local different solution. In particular the oxygen concentration may vary over the metal surface\textsuperscript{1}. This leads to a spatial separation of the anodic and cathodic reaction as illustrated in figure 2.2\textsuperscript{a}. This corrosion process is usually described with a differential aeration cell or oxygen concentration cell\textsuperscript{1}. Differences in oxygen concentration are for example caused by a difference in the length of the diffusion paths for oxygen to reach the metal interface, e.g. due to the geometry as a result of a barrier of formed corrosion products\textsuperscript{2}. At the aerated part of the metal surface the cathodic current is larger and so more oxygen will be reduced than at the less aerated part, according to reaction 2.1. This reaction causes a rise in pH of the aerated solution and consequently the passivation potential and the critical passivation current density will be lowered. Subsequently the aerated part passivates while a less
Figure 2.2  Local corrosion of an uncoated metal in an electrolyte solution (a). The charge transport in the metal and the solution are shown: electrons in the metal and ionic transport in the solution. Potential drop between anodic and cathodic sites in the electrolyte solution is indicated. As the potential drop increases corrosion current decreases, i.e. corrosion is inhibited. An Evans diagram is shown in b).

aerated part of the metal surface will dissolve because passivation is impossible due to acidification. For aluminium the acidification is a result of the anodic reaction according to reaction 2.5 and the hydrolyse reactions\(^3\) (eqs. 2.6 and 2.7).

\[
\text{Al} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^{2+} + 2\text{H}^+ + 3\text{e}^- \quad (2.5)
\]

\[
\text{Al(OH)}^{2+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^+ + \text{H}^+ \quad (2.6)
\]

\[
\text{Al(OH)}^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3^+ + \text{H}^+ \quad (2.7)
\]

The aerated part of the metal surface is thus protected by (re)passivation while the less aerated part is attacked.

In figure 2.2\(^a\) it is shown that electronic conduction occurs within the corroding metal and ionic conduction within the aqueous electrolyte solution. Due to the finite value of the resistance of an electrolyte solution, a potential drop exists between the anodic and the cathodic site. The effect of a potential drop on the
corrosion current is shown in figure 2.2 for the reactions discussed at general corrosion. When the potential drop increases, the cathodic site becomes smaller and so the cathodic current diminishes. Hence the corrosion current decreases. This is known as resistance inhibition\textsuperscript{4,5}. Since electrolyte solutions are highly conductive resistance inhibition is of minor importance for the corrosion of uncoated metals but for corrosion of coated metals it may considerably effect the corrosion rate as is discussed in the next section.

Figure 2.3 Polarisation curves of aluminium in acidic, neutral and alkaline solutions.

Experimental polarisation curves of aluminium are shown in figure 2.3. The anodic curves are more complicated compared to the anodic curve for bare metal surfaces shown in the Evans diagram (fig. 2.1). The reason for this is that a passive oxide film is covering the aluminium. It should be noted that the axis are exchanged.

2.2 Corrosion protection by coatings
The corrosion protection of metal substrates by organic coatings is attributed to a barrier mechanism, resistance inhibition, and/or an active inhibitive mechanism.

Barrier mechanism
Corrosion reactions can only take place if an electrochemical double layer is established at the metal-coating interface. Water and oxygen must be supplied through the coating. Organic coatings have often been described as physical barriers for water and oxygen. In literature this is referred to as the barrier
mechanism of the coating. The degree to which transport of water and oxygen to the metal-coating interface is reduced can regarded as a measure of the effectiveness of the coating in preventing corrosion. This idea induced a lot of research in order to characterise the barrier properties of organic coatings. The results of this research made clear that all coatings are permeable to water and oxygen to some extend. Consequently the barrier properties can not alone account for the protective action of a coating.

Resistance inhibition

Besides the oxygen permeability of the coating resistance inhibition may also play a role in corrosion protection. Resistance inhibition may take place because the anodic and cathodic reaction are spatially separated at the metal-coating interface. A path of high resistance between anodic and cathodic sites may exist which results into a reduction of the local corrosion rate.

Active inhibitive mechanism

The pigments can be divided into three groups: Passivating pigments, Galvanic pigments and Blocking pigments. Active pigments, i.e. passivating and galvanic pigments as for example chromate's or zinc pigments, provide addition corrosion protection through an inhibitive mechanism. In this thesis the role of these pigments will not be studies. It should be noted the presence of pigments effects as well as the adhesion properties and the oxygen permeation properties as the water absorption of a coating.

The corrosion protection of conversion layers on aluminium can be ascribed to the mechanisms described above: barrier and active inhibitive mechanism. Chromate conversion layers generally contain Cr(VI) species which can be reduced at places on the metal surface where the oxide layer has been damaged, resulting into a repassivation of the surface.

2.3 Mechanisms of coating failure

2.3.1 Initiation of blisters

Corrosion of metal substrates under intact or defective organic coatings is a very complex phenomenon. Underfilm corrosion may start from blisters which initiate at sites where the adhesion of the coating has been lost. Hess evaluated most types of irregularities. These sites may already be present directly after
application due to poor surface pretreatment, bad curing or handling the coating. Examples are cutting edges, edges of the construction which are always poorly covered by a paint, and salt rests of the pretreatment and other substances left on the metal surface. The salt particles prevent wetting by the coating which results in non adherent areas in the substrate-coating interface region.

Defects can also be caused by interaction of the coating system with its environment. The adhesion strength of a coating to its substrate is reduced significantly when the coating is immersed in water. This phenomenon is called: wet-adhesion. Water molecules at the metal-coating interface will weaken and finally break the cohesive bonds between the substrate and the polymer. The reduction of the adhesion strength as a function of the relative humidity of the atmosphere has been studied and showed a constant strength until high values of the R.H.. Near saturation of the coating, when water is condensed at the metal-coating interface, a remarkable drop is observed$^{11,12}$. From these results it is concluded that chemical adhesion is strongly related to the presence of condensed water at the metal-coating interface. It should be noticed that chemical adhesion is an extremely variable quantity which depends on the substrate, surface preparation, the coating type and the age of the coating$^{12}$.

![Graph showing weight gain versus decrease of adhesion strength.](image)

**Figure 2.4** The weight gain of coatings after 5 days during immersion versus the measured adhesion strength (%) under immersion. Weight gain is corrected for the pigment volume concentrations (PVC) by multiplying the weight gain given in the publication, with a factor $(1-\text{PVC})^{11}$.

(1) melamine epoxy, (2) thermosetting acrylic, (3) styrene butadiene, (4) polyamide cured epoxy, (5) epoxy ester, (6) polyurethane, (7) alkyd.
Another phenomenon which causes adhesion loss is swelling of the coating\textsuperscript{13}. Swelling occurs due to water absorption. As a consequence stresses may be built up in the interfacial region which result into the disruption of the adhesion. Verification was not found in an expected relation between the decrease of the adhesion strength and the water absorption of a coating. However, when the relative reduction of the adhesion strength is taken after 5 days, the adhesion trends to decrease with increasing water uptake (fig. 2.4). Assuming that water absorption leads to swelling and hence to adhesion loss, it is concluded that the more water a coating absorbs the more corrosion initiation sites are created.

\textbf{2.3.2 Blister growth}

The size of a blister is initially very small but a blister can grow as a result of a number of different phenomena. Funke\textsuperscript{15} evaluated mechanisms of blister growth of intact coatings under immersion. The most important mechanism is osmotic blistering due to high salt concentration at the interface. The osmotic process takes place if the coating is semi-permeable, i.e. permeable for water but impermeable or at least strongly retarding for ionic species. Organic coatings are almost impermeable for ionic species. The diffusion coefficients of ionic species are about a factor 1000 smaller than that of water\textsuperscript{16-19}. Large osmotic pressures may build up, like about 2.5 $10^5$ Nm\textsuperscript{-2}\textsuperscript{15}. Permeation rates through a coating measured from permeation experiments were compared with the rates of water transport necessary for the volume increase of the growing blister\textsuperscript{20}. The results of these measurements did indicate that the osmotic mechanism could account for most cases of blistering.

Different stages of blistering are schematically shown in figure 2.5. In the blister, corrosion reactions take place because water and oxygen are present. This will hardly influence the delamination at the edge of the blister but indirectly, when the electrolyte concentration increases, it enlarges the driving force for the build up of osmotic pressure. Depending on the mechanical properties of the coating, the coating may not withstand the high osmotic pressures and hence it will collapses. The corrosion mechanisms then directly contributes to a further loss of adhesion.
2.3.3 Cathodic delamination and anodic undermining

In literature two mechanisms are proposed which describe the propagation of underfilm corrosion in case of intact and defective coatings. These mechanisms are cathodic delamination and anodic undermining. At cathodic delamination the adhesion of the coating fails and causes lateral blister growth (delamination) as a result of a high pH \(^{21-23}\). The loss of adhesion at anodic undermining is caused by the dissolution of the metal or the metal oxide beneath the coating\(^3\). These mechanisms are also important in order to understand the mechanism of filiform corrosion which is described in part IV.

The cathodic delamination and anodic undermining mechanisms are the result of a differential aeration cell. Separation of anodic and cathodic reaction sites takes place in different ways depending on the oxygen transport path to the metal interface. The path is also determined by the fact whether the coating is intact or
defective. With intact coatings, oxygen is supplied through the coating or through both coating and formed solid corrosion products as schematically shown in figure 2.6. The length of the oxygen transport path to the interface at the edge of the blister is shorter compared to that at other places in the blister where oxygen also has to diffuse through the corrosion products. According to the differential aeration cell theory, the cathodic reaction will occur at the edge of the blister and the anodic reaction in the centre of the blister as shown in figure 2.6.

![Diagram showing oxygen transport paths in a blister]

*Figure 2.6  Oxygen transports paths in a blister in case of an intact coating. The resulting anodic and cathodic sites are shown in the figure. The transport paths for oxygen are shown.*

The separation of the anodic and cathodic reaction sites in figure 2.6 can be promoted by the nature of the corrosion products. When corrosion products consist of species which can be oxidised, oxygen is reduced during the transport through the corrosion products. The oxygen transport rate through the corrosion products will collapse and in the centre of the blister less oxygen will reach the metal surface. An example is the formed corrosion product of iron which initially mainly consists of Fe(II). Fe(II) will be oxidised to Fe(III) and will therefore reduce the oxygen\(^{7,24}\). Because the solubility product of Fe(III) hydroxides-oxide is very low, a porous solid film is formed. The proceeding corrosion process leads to film growth at the centre of the blister, which hinders the oxygen transport at the centre effectively.

From the discussions above it is concluded that the blister under intact coatings grows due to cathodic delamination independent of the metal substrate.

When defective coatings are considered, the situation is much more complex. Part of the substrate is now directly exposed to the corrosive solution. Corrosion will initiate at the defect and subsequently the formed corrosion products will block...
the pore. Corrosion propagation depends on the nature of the corrosion products in the pore. These stages are shown in figure 2.7a and 2.7b.

![Diagram showing corrosion initiation at defective coatings and blocking of the pore.](image)

*Figure 2.7  a) corrosion initiation at defective coatings, b) blocking of the pore. Initial loss of coating adhesion at the edges of the pinhole is shown*

The anodic undermining and cathodic delamination mechanism occurring at defective coatings depends on the ratio of the transport rates of oxygen through the coating and that through the formed corrosion products. Exceeds the oxygen rate through the coating that through the corrosion products the mechanism is cathodic delamination; The opposite leads to anodic undermining.

If the corrosion products contain no species which can be oxidised (e.g. with aluminium), the oxygen transport rate through the hydroxide-oxide corrosion products is estimated to be about 10⁴ times larger compared to that through an equal thick intact coating. As a consequence a blister grows due to anodic undermining (fig. 2.8a). Figure 2.8b shows the oxygen transport rates when the corrosion products can be oxidised as is the case with steel substrates. The Fe(III) products are represented as an additional layer in the figure. As discussed before the propagation mechanism in this case is cathodic delamination.

In literature the cathodic sites are sometimes positioned outside the blister as shown in figure 2.8c. In fact this case is equivalent to figure 2.8b. The reason for this is that a gradual transition exists between the delaminated area (the blister) and the well adherent coating and hence the exact position of the edge of the blister could not be observed accurately. As a consequence a cathodic site seems to be positioned outside the blister but it is in reality a part of the blister.
Figure 2.8  a) anodic undermining, b) cathodic delamination, c) cathodic delamination mechanism according to Funke$^{13}$. Oxygen transport paths are shown for both mechanisms. Fe(III) corrosion products are represented as an additional layer in b) and c).
2.3.4 Oxygen transport in case of cathodic delamination

The cathodic delamination mechanism on coated steel substrates has been subject of many investigations. Since an enormous pH gradient is expected due to the spatially separated corrosion reactions it was tried to measure the pH locally. The pH is found to be highly alkaline at the edge of the blister, where the oxygen reduction reaction (eq 2.3) takes place. Ritter et al.\textsuperscript{26} reported that the pH at the delaminating edge is greater than 14 as measured by pH-sensitive electrodes inserted through the metal substrate from the back side. The solution in the blister is very acid as was concluded from the observed etched area.\textsuperscript{27}

In case of cathodic delamination the oxygen for the cathodic reaction is supplied through the coating. To obtain insight into the importance of the oxygen supply, oxygen transport rates through a coating were compared with the amount of oxygen needed for an observed corrosion rate of coated and uncoated substrates. Wormwell\textsuperscript{28} and Boxal\textsuperscript{29} examined corrosion rates of uncoated mild steel in aerated sea water and in industrial environments (atmospheric corrosion). They reported that an oxygen amount of 0.010 to 0.025 mg day\textsuperscript{-1} cm\textsuperscript{-2} was consumed. This amount can not be supplied through organic coatings. The results from permeation experiments showed that the oxygen supply through 100μm thick dry coatings was only 0.005 to 0.015 mg day\textsuperscript{-1} cm\textsuperscript{-2} \textsuperscript{15,30,31}. From these results it is concluded that the corrosion rate may be controlled by the oxygen supply through the coating (\textit{barrier mechanism}).

It is generally accepted that the produced hydroxide ions at the oxygen reduction reaction lead to delamination of the coating. As discussed the rate of this reaction is controlled by the oxygen supply through the coating. As a consequence the permeation properties of the coating are related to the delamination rate. The oxygen supply is suppressed by applying an extra coating film onto the coating surface around the defect.\textsuperscript{32} The delamination rate of the coating was found to reduce significantly.

Leidheiser\textsuperscript{33-35} did a lot of experiments at cathodic potentials between -800 mV to -1000 mV (SCE) with both uncoated and coated steel substrates at which in the latter case the coating contain a pinhole. In this narrow cathodic potential range the dominant reaction is the oxygen reduction reaction which is found to be diffusion controlled\textsuperscript{34}. It is found that the delamination rate is independent of the applied cathodic potential. Varying the oxygen concentration in the solution effects the oxygen rate through the coating which can be described by the
Fickians first law. When the concentration gradient of oxygen increases, the rate of the oxygen transport through the coating and so the delamination rate would increase. A linear relation was found between the delamination rate and the oxygen concentration in the solution\(^7\,^{,\,34}\). It should be mentioned that in these experiments also some oxygen was supplied through the defect to the cathodic site in the edge of the blister.

According Fick's law, the oxygen transport through the coating is also determined by the coating thickness. A linear relation between the observed delamination rate and the coating thickness could be calculated from data in literature (fig. 2.9)\(^36\), indicating that diffusion through the coating controls the delamination rate. This relation has also been reported for a polybutadiene coating in a small thickness range of 10 to 20\(\mu\)m\(^35\). So it can be concluded from this figure that the delamination rate is indeed controlled by oxygen diffusion through the coating.

![Delamination rate vs. coating thickness](image.png)

*Figure 2.9  Delamination rate of a chlorinated rubber coating with pinhole (diameter 3 mm) on mild cold rolled steel. Sample has been cathodically polarised at -1050 mV SCE\(^36\). Slope is -0.91±0.15

### 2.3.5 Oxygen transport in case of anodic undermining

Figure 2.6\(^a\) showed that the oxygen transport at anodic undermining takes place via the defect. As a consequence it is independent of the coating properties. Corrosion protective action of an organic coating is thus not provided by the *barrier mechanism*. Hence the delamination rate would not be a function of the coating thickness. Unfortunately no data in literature are found to support this. However, from experiments of Koehler\(^37\) it is shown that aluminium is particularly
susceptible to anodic undermining. He sealed organic coated panels to opposite ends of a cylindrical cell filled with electrolyte. The two panels were connected to a power supply and a current of 0.09 μAcm⁻² was passed for a week. Underfilm corrosion was observed on the anodic panel while no corrosion damage was found on the panel which was the cathode.

2.3.6 Ionic transport phenomena between anodic and cathodic sites
A deposit is formed between the anodic and cathodic site since the solubility product of metal cation-hydroxide is quite small for most metals. During blister growth, the deposit will dissolve at the anodic site due to the low pH whereas at the cathodic site the deposit may growth²⁷. To complete the electrical circuit an ionic current will pass between the anodic and cathodic sites as was shown in figure 2.2a for uncoated substrates. In a blister this charge transport will also take place. Figure 2.10 shows schematically the ionic charge transport in case of coated steel and aluminium substrates, i.e. for cathodic delamination and anodic undermining. Both the anion and the cation may contribute to the ionic current. When this transport is hindered, the corrosion rate diminishes and hence the corrosion protection is provided by resistance inhibition.

Auger Spectroscopic measurements (AES) have been performed in the blister on coated steel substrates³⁴. For this goal a defective coating was exposed to an aerated 0.5 M KCl solution at the corrosion potential. After removing the coating, the surface was analysed by AES at the blister area. The potassium-chloride ratio was 12.5, indicating the preferential diffusion of cations to the cathodic delaminating region. Therefore the cation transport to the edge of the blister, may also effect the delamination rate of a coating.
For defective coatings the cations involved in the charge transport process, originate from the electrolyte solution. Different type of cations may diffuse at different rates to the edge of the blister because their diffusions coefficients in water differ. This results into different delamination rates which is confirmed experimentally. A linear relation exists between the delamination rate and the diffusion coefficients of LiCl, NaCl, KCl, CsCl, and CaCl₂ in water, indicating that cation diffusion controls the delamination rate³⁵. Experiments of Stratmann using the Kelvin method³⁸-⁴⁰ confirm this result.
For anodic undermining the ionic transport is assumed to be mainly anionic. This is attributed to the fact that the concentration of free metal cations is small.

\[ \text{O}_2 \quad \text{coating} \quad \text{Fe(III) deposit} \quad \text{Fe}^{2+} \quad \text{Na}^+ \quad \text{OH}^- \quad \text{substrate} \]

\[ \text{coating} \quad \text{deposit} \quad \text{Al}^{3+} \quad \text{Cl}^- \quad \text{OH}^- \quad \text{O}_2 \quad \text{substrate} \]

Figure 2.10 Schematical representation of the ionic charge transport between anodic and cathodic sites for coated steel (a) and aluminium (b) substrates. Oxygen supply is also shown for both metals.

The anion transport to the edge of the blister may be harmful because it often concerns aggressive anions as chlorides. Chloride ions cause local attack of the oxide layer in the edge of the blister and hence this may accelerate the corrosion rate. Anions also forms complex ions with the metal cation. The free metal cation concentration is then considerably smaller. This leads to a more negative
equilibrium potential for the anodic reaction and consequently the corrosion process may be accelerated.

2.4 Conclusions
Local corrosion on intact coated metal substrates starts with osmotic blistering at sites at the substrate-coating interface where adhesion loss occurs. For prevention, special attention must be paid to the procedures of preparing a sample. Sites of bad adhesion must be avoided. Consequently, contamination of the substrate surface with salts or oxides, left after cleaning procedures, should be avoided. The presence of salts may also facilitate osmotic processes and is therefore quite harmful. A final rinse of the surface with de-ionised water may reduce the number of hygroscopic salt particles left at the substrate-coating interface. Hence the initiation of corrosion is retarded. The water absorption behaviour of a polymer, which leads to stresses in the coating, may induce adhesion loss at the coating-substrate interface and may result in initiation sites. The adhesion properties of the coating-substrate system (chemical, mechanical and wet adhesion) are of major importance for the rate of osmotic blistering. Depending on the mechanical properties of a coating, the coating may either sustain the osmotic pressure or not.

Often the coating has been damaged. In this case no osmotic blistering occurs. The blister is leaky and no osmotic pressure can be built up. After certain time a differential aeration cell has been established due to different diffusion path lengths for oxygen. Depending on the oxygen transport path, anodic undermining or cathodic delamination may occur. For anodic undermining the oxygen is supplied through the coating defect whereas for cathodic delamination the oxygen is supplied through the coating. Consequently the oxygen permeation properties of a coating are important for the propagation rate of the corrosion process in the latter case. For effective corrosion control, the rates of the cathodic reaction for cathodic delamination or the anodic reaction for anodic undermining should be retarded. In case of coated aluminium substrates (anodic undermining) the propagation of corrosion phenomena is indeed considerably retarded by pretreatment layers as phosphatised, bömited, anodised and chromatised conversion layers. In the latter case also electrochemically active pigments in the conversion layer are present, i.e. Cr(VI). Contamination of the coating defect with salts (e.g. at sea coasts) may considerably accelerate corrosion since it reduces
the conductivity between the spatially separated anodic and cathodic site. Regular cleaning of a coated surface should retard corrosion phenomena. Finally, figure 2.12 shows schematically the main factors in corrosion mechanisms of coated substrates. It includes also the proposed corrosion protection mechanisms by organic coatings, i.e. the barrier mechanism, the resistance inhibition, and the active inhibitive mechanism.

**Corrosion mechanisms of coated substrates**

- Intact coating,
  - Local adhesion loss of the coating at the coating-substrate interface

**Osmotic blistering**

- chemical and mechanical adhesion of the coating
- contamination of the coating-substrate interface with salts
- water absorption in the coating

**Mech. prop. of the coating**

Coating remains intact during undetfilm corrosion process

**Differential aeration cell**

- oxygen supply through the coating near the edge of a blister

**Cathodic delamination**

- presence of electr.chem. active pigm. in coating or conv. layer

- contamination of the coating-substrate interface with salt

- Primary effects:
  - the rate of the oxygen reduction reaction at the substrate-coating interface and the oxygen permeation properties of the coating

- Secondary effects:
  - the chemical adhesion properties of the coating
  - ionic conductivity between the anodic and cathodic site

**Anodic undermining**

- inhibition of the reactions

- barrier mechanism

- resistance inhibition

- Primary effects:
  - the rate of the anodic reaction at the substrate-coating interface

- Secondary effects:
  - the adhesion properties of the coating
  - the formation of complex ions with the metal cation
  - ionic conductivity between the anodic and cathodic site

**Figure 2.12 Corrosion mechanisms of coated metal substrates**
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Chapter 3

CORROSION MECHANISMS OF FILIFORM CORROSION

3.1 Introduction
In this chapter a literature review of filiform corrosion is given. The results of research on mechanisms for filiform corrosion are confusing. This is mainly caused by the fact that no effort is done to relate the well-accepted delamination mechanisms as anodic undermining and cathodic delamination, to the experiments carried out. On the other hand several factors which might cause filiform corrosion have been examined. Hence the practical conditions for filiform corrosion to occur are known reasonably well. As mentioned in chapter 1, the following four conditions have been reported in literature\textsuperscript{1-10}:

- an atmosphere of high relative humidity,
- permeability of the coating for water and oxygen,
- contamination at the coating-substrate interface with salts,
- the presence of defects in the coating.

The conditions mentioned before cover both the initiation and propagation stage of filiform corrosion and need not necessarily apply at the same time. In the next sections 8.2 and 8.3, initiation and propagation of filiform corrosion are reviewed. A critical evaluation of available data was aimed at the establishment of a possible relation between the anodic undermining and cathodic delamination mechanisms, and the conditions mentioned above.
The effect of adhesion strength and different pretreatments of aluminium are discussed in section 8.4. Finally some conclusions are given in section 8.5.

3.2 Initiation of filiform corrosion
In this section the influence of various parameters on the initiation of filiform corrosion is discussed. In building filiform corrosion often occurs at window frames. Filiform corrosion at these construction parts does always initiate within the first two years of outdoor exposure\textsuperscript{11}. After this period no filiform corrosion
damage is generally found to occur anymore. This shows that the initiation is very important.

The initial stage of filiform corrosion is the initiation of blisters which successively turn into filaments. This is clearly observed by a few authors like van der Berg\textsuperscript{12} and Barton\textsuperscript{13}. Photographs in references 3 and 8 show also blisters as initial step in the filiform corrosion mechanism.

Blister initiation has been discussed in chapter 1. As discussed a defect at the metal-coating interface is required for initiation. Filiform corrosion initiates most easily at sites where an organic coating is mechanically ruptured and discontinuous. An example is a cutting edge\textsuperscript{1,4,14}. Another type of defect is adhesion failure due to the presence of salt particles originally left on the metal substrate before the application of the coating\textsuperscript{1,14}.

A blister may grow just as a result of osmotic process or due to cathodic delamination or anodic undermining. When salt particles are present on the substrate-coating interface and when these are covered with an intact coating, osmosis results in blister growth. This process is slow in humid atmospheres since a large pressure has to build up before delamination takes place. These defects are thus less favoured as initiator points\textsuperscript{3}.

The number of initiation points for blisters is certainly related to the amount of salt particles present at the substrate surface. To validate this, surfaces have been contaminated before the application of the coating with electrolyte solutions of different concentration. The higher the concentration of the solution is (concentration range between $10^{-2}$ and $10^{-6}$ mol/l), the more filaments are indeed observed\textsuperscript{15}.

The presence of ionic species left on the substrate surface can also be caused by the pretreatment of the metal substrate. It is found that a reduction of the susceptibility to filiform corrosion can be obtained by giving a phosphatised substrate a final rinse in demineralized water\textsuperscript{16}. This improvement is ascribed to the removal of salts and hygroscopic materials from the surface. Finally ionic species can also be supplied by the coating. Vinyl coatings are well-known because of their chloride content\textsuperscript{8}. These coatings are very susceptible to filiform corrosion\textsuperscript{8}.

Mechanical defects like cutting edges are often polluted with salt from the atmosphere. Water and oxygen can be supplied very easily through the defect
and as a consequence the blister starts growing due to the mentioned corrosion mechanisms.

In literature the influence of the hygroscopic properties of many salts on the initiation of filiform corrosion is discussed in detail. The hygroscopic properties of a salt are given as an equilibrium value for the relative humidity in a closed space which also contains a saturated solution of the salt. Table 3.1 shows the values of the relative humidity for some salts\textsuperscript{17}.

In practice the relative humidity of the atmosphere differs from the humidity given in table 3.1. This means that at lower humidities water evaporates to the atmosphere and at higher humidities the salt absorbs water from the atmosphere. It is thus expected that the occurrence of corrosion in a humid atmosphere can be influenced by the hygroscopic properties of these salts.

<table>
<thead>
<tr>
<th>solid phase</th>
<th>R.H. (%)</th>
<th>solid phase</th>
<th>R.H. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium sulphate</td>
<td>93</td>
<td>sodium acetate</td>
<td>76</td>
</tr>
<tr>
<td>potassium chromate</td>
<td>88</td>
<td>ammonium chloride</td>
<td>71</td>
</tr>
<tr>
<td>potassium chloride</td>
<td>86</td>
<td>magnesium sulphate</td>
<td>65</td>
</tr>
<tr>
<td>ammonium sulphate</td>
<td>81</td>
<td>calcium chloride</td>
<td>32</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>78</td>
<td>lithium chloride</td>
<td>15</td>
</tr>
</tbody>
</table>

*Table 3.1 Hygroscopic properties of salts at 20 °C*\textsuperscript{17}.

Preston et al\textsuperscript{14} examined atmospheric corrosion of *uncoated* metal surfaces which were contaminated with different salts. They measured the weight gain of the samples and observed no weight gain as long as the relative humidity remains below the equilibrium value of the humidity of the initiating salt, given in table 3.1. At these R.H. no electrochemical double layer can be built up and hence no corrosion occurs.

The relation between filiform corrosion and the hygroscopic properties of the salts is still a matter of discussion. All research in this field was performed on contaminated metal surfaces which were coated after contamination of the surface. A fair relation between the hygroscopicity of the initiating salt and the onset of filiform corrosion was noted for ammonium chloride, sodium chloride and sodium sulphate\textsuperscript{15,18}. Other salts are more or less controversial. It should be noted that metal cations of a contamination as magnesium cation result in a
hydrolysis reaction and will consequently reduce the pH considerably. This may stimulate a local corrosion attack of the metal surface. Ruggeri\textsuperscript{4} suggested that not the initiating salt determines the initiation of filiform corrosion but the salt of the metal cation and the anion of the initiating salt (mostly chloride salts). The relative humidity of iron chloride salts is about 58% R.H. This value agrees quite well with the experiments\textsuperscript{4, 18}. No filaments on steel substrates grow below 60% R.H.. Slabaugh\textsuperscript{1} initiated filiform corrosion on aluminium with hydrochloric acid and observed growth down to 30% R.H. at 40°C. An equilibrium value for the R.H. of about 34 is given for a aluminium chloride salt.

Let us now return to blister growth and propagation of filiform corrosion. The transition from blister to filament is still not clear. From both laboratory and field studies it is evident that, once a filiform is induced, it grows independently of the method by which it was initiated\textsuperscript{6}.

3.3 Propagation mechanism of filiform growth
In this section the propagation mechanisms of filiform corrosion on both aluminium and steel substrates are discussed. The differential aeration cell plays an important role in the mechanisms\textsuperscript{4}. When oxygen was excluded from the environment by purging with inert gases like helium, nitrogen and argon, filiform corrosion was inhibited on both coated aluminium and steel substrates\textsuperscript{7}. Moreover the filiform growth rate has been seen to increase with increasing concentration oxygen in the atmosphere.

The propagation mechanisms of filiform corrosion are similar to the mechanisms of blister growth as discussed in chapter 1, i.e. anodic undermining and cathodic delamination. Depending on the transport path of oxygen to the active head of the filament, either anodic undermining or cathodic delamination occur. In case of anodic undermining oxygen is supplied through the tail of the filament whereas the oxygen transport in case of cathodic delamination takes place through the coating. In the latter case the propagation mechanism depends on the permeation properties of the coating. In chapter 1 it has been demonstrated that the blister growth mechanism is determined by the nature of the substrate. For filiform corrosion this is also valid. At coated steel Fe(II) species in the tail of a filament are further oxidised, resulting in an effective barrier for oxygen transport to the active head. The corrosion products of aluminium, however, do not contain active species and are therefore considerably permeable.
for oxygen. Clearly, similar as for blistering, anodic undermining occurs at coated aluminium and cathodic delamination at coated steel substrates. In section 3.3.1 the mechanisms are discussed in more detail for filiform corrosion.

The four conditions for filiform corrosion, mentioned in section 3.1, are now evaluated in relation with the propagation of filiform corrosion. The effect of oxygen on the growth rate of a filament is evaluated in section 3.3.2 for coated steel and in section 3.3.3 for coated aluminium substrates. The effect of carbon dioxide is shortly reviewed in section 3.3.4. Subsequently the water transport to the filiform head is discussed (section 3.3.5). Finally the influence of ionic species on the propagation rate is given in section 3.3.6.

3.3.1 Cathodic delamination and anodic undermining in case of filiform corrosion

The often proposed cathodic delamination mechanism for coated steel substrates\(^7\) is shown in figure 3.1.

![Diagram of cathodic delamination mechanism](image)

*Figure 3.1* Cross sections of the cathodic delamination mechanism on coated steel substrates\(^7\). The position of the cathodic and anodic sites, as well as the oxygen and water supply are shown.
Funke\textsuperscript{15} proposed a different cathodic delamination mechanism which is shown in figure 3.2. The cathodic site where oxygen is reduced, is positioned in front of the filament. Since ionic diffusion through a coating is a very slow process the position of cathodic areas outside the filament suggests that the adhesion is bad. Ionic transport must pass through the interfacial region between substrate and coating to complete the circuit. The successive stages of filiform growth are schematically shown in figure 3.3. Both the cathodic spots in front of the filament and the anodic front of the filament head will grow in time until they join and the process will start again. In chapter 1 a similar discussion on the position of the cathodic reaction is given for blisters. From this, it has been concluded that a cathodic site outside a blister is less likely and hence a cathodic site in front of a filiform. The mechanism of Funke is thus not considered furthermore.

\textbf{Figure 3.2} Cross sections of the cathodic delamination mechanism according to Funke\textsuperscript{15}. The position of the cathodic and anodic sites as well as the oxygen and water transport paths are shown.
Figure 3.3  The mechanism of cathodic delamination according to Funke\textsuperscript{15}.

The anodic undermining mechanism on coated aluminium substrates is schematically shown in figure 3.4. The transport path of oxygen through the tail of the filament is indicated in the figure. Studying the rate of the oxygen supply through a coating and that through a porous oxide in the tail of the filiform it was found that diffusion through the porous oxide was most likely\textsuperscript{4}. This confirms the ideas of Kaesche\textsuperscript{18} who suggested that the filament tail was an important path. He did not present mathematical or experimental verification. Since the anodic site is positioned at the front of the filament head (fig. 3.4) Slabough\textsuperscript{2} suggested that the rate of filiform corrosion on coated aluminium might depend on the rate of the anodic reaction.
Figure 3.4 Cross sections of the anodic undermining mechanism on coated aluminium substrates. The anodic and cathodic sites as well as the oxygen and water paths are indicated.

The pH in the head of the filament would provide direct evidence for the different delamination mechanisms on coated steel and aluminium alloys. However, one should be very carefully and do the pH measurement at the very narrow edge of the delamination in order to obtain evidence for the mechanism. An alkaline front in the filiform head (pH=10) has been observed at coated steel substrates, pointing at cathodic delamination\textsuperscript{7,10,19}. Some authors report results of pH measurements in the head of the filament in stead of the narrow edge. The pH is found to be low\textsuperscript{3,5,12}.

The delamination rate on coated steel substrates can be effected by rests of acids in a coating. These species neutralise the hydroxide ions present at the edge of the filament. As a consequence the saponisation of the coating is slowed down, resulting in a smaller delamination rate. This is for example the case for (acid cured) acrylic coatings\textsuperscript{20}. The oxygen permeability of acrylic coatings is generally large, leading to a large delamination rate\textsuperscript{20}. However, filiform corrosion is considerably retarded compared to coating systems with similar oxygen permeation properties. The retardation can be attributed to acid rests in the coating.
pH measurements in the filament head at coated aluminium alloys showed that the front is acidic\textsuperscript{1,4,7,9}. Hoch\textsuperscript{6} observed acid areas around the filiform head when she mixed a very sensitive pH indicator through a primer resin before application. Clearly, the mechanism of filiform corrosion for coated aluminium is anodic undermining. Further evidence for this mechanism was found by microscopic examinations\textsuperscript{1,5,9} which showed that gas bubbles were formed in the filament head. Because of an acid front these gas bubbles were assumed to be hydrogen gas bubbles. It should be noticed that hydrogen gas has not been detected analytically.

3.3.2 Oxygen transport in case of coated steel substrates
According to the cathodic delamination mechanism (section 3.3.1) the filament growth rate should be controlled by the oxygen transport through the coating, i.e. by the permeation properties of the coating for oxygen. In literature a considerable number of coating types has been examined for their permeation properties, like epoxy-amine, polyurethane, alkyd and phenol coatings, acrylic lacquers, vinyl copolymers, often both clear and pigmented\textsuperscript{1,2,13,20}. Filliform corrosion occurred for all coatings and therefore many scientists assumed that the type of coating was not critical\textsuperscript{1,2,13}. However, it was clear that some binders perform better than others in filiform corrosion tests\textsuperscript{9,21}. Polyurethane coatings for example are slightly more effective in controlling filiform corrosion than other coating systems like epoxies, polyesters and alkyds\textsuperscript{1}. This is due to the fact that the oxygen permeability of this coating is about a factor ten to forty smaller\textsuperscript{22} than the permeability of the other coatings mentioned.

The pigment volume concentration (PVC) determines also the oxygen permeation properties of a coating. It has been found that the rate of oxygen diffusion decreases markedly with the pigment volume concentration\textsuperscript{22,23,34}. This leads indeed to a lower susceptibility of filiform corrosion\textsuperscript{1,2}.

Let us now look more carefully. The growth rate of a filament should be constant for a certain coating, independent on the filament length. This has been observed for exposure times until 85 days\textsuperscript{4,14} as shown in figure 3.5 for steel substrates. Different coatings have different growth rates (fig. 3.5\textsuperscript{b}), illustrating the influence of the permeation properties of the coating on the filament growth rate.
Figure 3.5  The length of a filament on coated steel substrates as function of the exposure time. The slopes yield the constant growth rates of the filaments for these samples

a) ○ CaCl₂ initiating salt, rate: 1.9 mm day⁻¹ and ● NaCl initiating salt, rate : 3.8 mm day⁻¹ (1).

Zapon coating at 25°C and 85% R.H. Figure is directly adopted from reference 18.

b) ○ 5.6 μm thick vinyl coating, rate: 9.6 × 10⁻³ g day⁻¹ and ● 8.6 μm thick polyisobutylene coating, rate: 19.3 × 10⁻³ g day⁻¹. Conditions are 20°C and 86% R.H.. Figure made from data sets given in reference 7.

c) varnish on steel, rate : 1.8 × 10⁻¹ mm day⁻¹. Figure is directly adopted from reference 14.

Humidity and temperature were those normal to an indoor atmosphere in winter.

(1) The growth rate of a filament (i.e. slope) is also influenced by the type of the initiating salt. This is discussed in section 3.3.6.
Ficks first law describes the oxygen transport through a coating. Assuming that oxygen is completely consumed at the substrate interface, two simple predictions based on Ficks first law are obtained. Firstly the oxygen transport diminishes with a decreasing concentration gradient. The gradient increases with decreasing coating thickness and increasing activity of oxygen in the coating. Secondly the transport diminishes with smaller values of the diffusion coefficient of oxygen in the coating. If filiform corrosion is controlled by oxygen diffusion through the coating, the growth rate of the filaments is determined by the oxygen supply. Hence the growth rate should diminish with increasing coating thickness, with a decreasing activity of oxygen in the coating and with a decreasing value of the diffusion coefficient.

These relations are found in literature. The growth rate increases with the oxygen concentration in atmosphere\(^7\), i.e. with increasing oxygen activity in the outer coating layer according to Henry's law. A considerable decrease of the growth rate is found when the coating thickness increases\(^20\) or when the filiform head is sealed with an extra layer epoxy coating\(^4\). In both cases filiform corrosion is not inhibited completely because there still exists an definite oxygen supply. Van Loo\(^2\)

\[\text{Figure 3.6  The corrosion rate as a function of the coating thickness, calculated from data sets, given in literature}^{(1)}. \text{ Slope is } -2.0\pm0.2.\]

\(^{(1)}\) the corrosion rate was calculated from the filiform growth, the width and the corrosion depth into the metal. For the data of Holler the length of the filament was determined. A constant growth rate was assumed. Missing data needed for the calculation were estimated from the figures and photographs or else a mean value was taken from the survey of Ruggen\(^4\).

reports that the growth rate of the filament is constant in a region of constant thickness (constant permeability) and that the filament tends to bounce away from
areas which have a much larger coating thickness (smaller permeability). Our experiments confirm this. Moreover the experiments showed that the filament grows in the direction of the smallest coating thickness and so in the direction of the largest oxygen supply through the coating.

From data on filament growth in literature, the growth rate of a filament as a function of the coating thickness has been calculated and is shown in figure 3.6. Because of differences between steel alloys, pretreatments, and conditions of exposure, it is not surprisingly that the slope in figure 3.6 deviates from the value -1, predicted by Fick's first law. In addition it should be noted that the coating over the filament head is stretched which inevitably leads to deviations from Fickian diffusion behaviour. The linear relation only indicates that the oxygen transport plays an important role for the growth rate of the filaments.

The cathodic delamination mechanism is exclusive for coated steel substrates. When the transport path for oxygen through the coating is limited by applying a very thick coating, the normally small oxygen supply through the tail may become relatively important. This results then in an anodic undermining mechanism. An example is given by Ruggeri et al\textsuperscript{4}. They applied very thick polyurethane coatings (at least 3 mm) on steel substrates. These coatings are considerably thicker than usually used in filiform corrosion tests (factor 30) and are known to have very low permeability for oxygen\textsuperscript{22}. The anodic undermining mechanism and the oxygen transport through the tail was validated by sealing the defect from which the filiform had been initiated. The growth rate of the filiform was indeed retarded considerably\textsuperscript{4}.

3.3.3 Oxygen transport in case of coated aluminium substrates

According to the anodic undermining mechanism the oxygen is supplied through the tail of the filament. Therefore the growth rate may depend on the length of the tail of the filament and diminish with increasing length of a filament. To validate this, the filament length as a function of the exposure time has been determined for several coatings reported in literature\textsuperscript{5,6,24}. While the filaments are still relatively small at short exposure, sufficient oxygen can be supplied, resulting in a constant growth rate (fig. 3.7a). As expected for long exposure times the rate of filament growth slows down which is clearly seen in figure 3.7b for a polyester coating. The typical shape of the curve is also found for acrylic and polyurethane coatings on both degreased and anodised alloys.
Figure 3.7 The length (or area) of a filament on coated aluminium substrates as function of the exposure time. a) clear primer and polyurethane top coating on aluminium (30µm thick) exposed at room temperature and 75% R.H. Rate : 0.14 mm day⁻¹. Data were estimated from photographs in reference 5. b) polyester coating on anodised aluminium alloys at 40°C and 80% R.H. Figure is directly adopted from reference 24.

It is clear at first sight that the oxygen transport paths are different for aluminium and steel substrates. As has been discussed before, the length of a

Figure 3.8 The length of filaments on steel (¹) plotted versus that on aluminium substrates for 15 different chemical cured coating types after 42 days of exposure at 85% R.H. and 25°C⁹. Initiation occurs by an exposure to hydrochloric acid vapours for one hour. The thickness of all coatings is 32±5 µm.

(¹) The length of the filiform was given after 33 days of exposure. Because the growth rate is constant (fig. 3.4) the length of the filiform has been adjusted to that of 42 days of exposure by extrapolation.
filament is proportional to its constant growth rate for both substrates. However, in case of aluminium substrates this is only valid as long as the length of the filaments is relatively short. Moreover the growth rate on coated aluminium substrates is independent on the permeation properties of the coating for oxygen. Differences in filament length on aluminium substrates are resulting from experimental artefacts. For coated steel however the growth rate is determined by the permeation properties of the coating. Hence for steel the oxygen diffusion through coatings and the growth rate of a filament can be controlled by selection of the coating type. The different behaviour of aluminium and steel substrates becomes obvious in figure 3.8, where the length of filaments on both substrates for different coatings after a fixed exposure time is given.

3.3.4 Carbon dioxide
Carbon dioxide may effect filament growth rate, depending on the metal substrate\(^7\). It has been found that on steel substrates the rate slows down considerably when a small amount of carbon dioxide is present in the atmosphere (<5\(^v\%\)). A concentration of carbon dioxide in the atmosphere of above 5 \(^v\%\) completely inhibits filiform corrosion on steel substrates. On aluminium alloys however no influence on the rate of filament growth has been observed\(^7\). In this section it is demonstrated that the influence of carbon dioxide on the growth rate of a filament is determined by the propagation mechanism.

If carbon dioxide is involved in a cathodic reaction the following reaction takes place:

\[
2\text{CO}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{HCO}_3^- \tag{3.1}
\]

The transport paths for carbon dioxide are similar to oxygen, i.e. through the tail in case of anodic undermining for coated aluminium alloys and through the coating in case of cathodic delamination for coated steel. Reaching the cathodic site bicarbonate ions (\(\text{HCO}_3^-\)) are formed which precipitate with ferrous and aluminium ions. In addition bicarbonate ions buffer the pH of the solution, in particular in alkaline solutions:

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \tag{3.2}
\]
So bicarbonate decreases the alkalinity, resulting from the oxygen reduction reaction at the cathodic site\(^4\). In case of cathodic delamination on steel substrates the delamination rate is slowed down. For the anodic undermining mechanism on aluminium however, the cathodic reaction of carbon dioxide does not effect the anodic reactions in the front, assuming that the transport paths for carbon dioxide and oxygen are similar. Hence the reaction has also not influence on the filament growth rate on aluminium.

### 3.3.5 The influence of water on filiform corrosion

The relation between the relative humidity of the atmosphere and the propagation mechanism of filiform corrosion is still not clear. There are reasons to believe that water transport to the head of the filament takes place through the coating. Figure 3.9 shows schematically the nature of the corrosion products in a filament. A highly concentrated electrolyte solution is present in the narrow edge of the filament head\(^2,3,6,10\). Furthermore it has been observed that the nature of the corrosion products in the tail varies from gel-like near the edge to dry stable products furtheron in the tail\(^10\). From the fact that the tail contains stable (dry) corrosion products it is concluded that no water diffuses through this medium. Hence the water transport to the filament head must occur through the coating.

![Figure 3.9 Different driving forces for water transport to the active head of a filament, i.e. osmosis and diffusion](image)


\(^7\) P. J. V. Pons: The role of cathodic reactions in the growth of filiform corrosion, Corr. Sci., 1977, 17, 647.


The different water transport processes, osmosis and diffusion, are also shown in figure 3.9 for a stationary situation. It should be noted that for osmosis a closed volume is required. The head however is leaking but for long filaments with dry and gel-like corrosion products in the tail this condition is approximately satisfied. In the tail of a filament osmosis must also take place. Corrosion products in the tail can only dried as result of osmotic water transport to the head.

In the edge of a filament where a saturated solution is present, osmosis mainly provide the water supply through the coating since the diffusion process is relative slow. The osmotic process only depends on the water activities on both sites of the coating, i.e. in the tail and in an adsorbed water layer on the coating surface. Therefore the water transport through the coating is not influenced by factors as the relative humidity of the atmosphere or the coating thickness. The solution in the edge will not dried out and as a consequence it may be expected that the growth rate does not depend on factors as the relative humidity of the atmosphere. The results in literature on the dependence of the R.H. on the growth rate are confusing. As well as a small increase as a decrease of the growth rate was reported for coated steel samples exposed under similar conditions, indicating that the suggested independence is reasonable.

Furtheron in the tail, where dry and stable corrosion products are present, water penetrates the coating as result of a diffusion process. The water concentration gradient in the coating, required for diffusion, is maintained because water in the tail is transported to the head by osmosis. The gel-like part may then be considered as a semi-permeable membrane.

In case of a very permeable coating, water is present at several sites at the substrate-coating interface. As a consequence underfilm corrosion may occur. The growth of the blisters will dominate the unidirectional growth of blisters into filaments. On the other hand, when the permeability of a coating increases from very low to larger values, it is expected that filament growth changes slowly to blister growth. So, the dimensions of the filament increases with increasing water permeability of the coating. At low relative humidities of the atmosphere (<50%) the adsorption process of a thin adsorbed water layer on a coating surface dominates the water permeation. In addition the activity of water in a coating, which is described by Henry's law, is small for coatings exposed to these atmospheres. Therefore the diffusion of water in a coating is slow, resulting in a slow overall permeation process. At high relative humidities however the
penetration of water in a coating is dominated by the diffusion process of water in the coating\textsuperscript{25}. It is then not surprising that the width of a filament tail increases with humidity\textsuperscript{1,2,4} and that near the saturation vapour pressure of water, the filaments broaden into blisters\textsuperscript{8}.

The permeability of a coating is determined by the critical pigment volume concentration, CPVC, the glass transition temperature $T_g$ and stresses in the coating. These factors are now discussed successively. It is evident that only below the CPVC of a coating filiform corrosion occurs. Above the CPVC, where there is an insufficiency of binder and therefore the coating is very porous, only blistering has been observed\textsuperscript{2}.

As discussed in chapter 5 the permeation of the coating increases considerably at temperatures above the glass transition temperature of the coating. The permeation process in the rubbery state of a polymer is usually described by ideal-Fickian diffusion. In the glassy state however the initial Fickian diffusion process can be retarded by relaxation processes in the polymer. Scheck\textsuperscript{24} shows in his thesis that the area of a filament which reflects the dimensions of a filament, depends considerably on the relative temperature $T/T_g$.

Finally it is well-known that water diffusion is retarded in case of stressed coatings. In part IV it is demonstrated that the water uptake in network polymers is retarded as a result of stresses that are built up when water enters the coating. For coatings over a filament however, deformation of the coatings occurs due to the formed corrosion products in the tail and as a consequence a stress is built up in the coating. In thicker coatings the stress is relatively lower and as a result the water permeation is less influenced. In literature it is found that the width of a filament slightly increases with an increasing film thickness\textsuperscript{2,18}.

3.3.6 The influence of ionic species on the growth rate
As has been discussed in part I, the corrosion rate in blisters is influenced by ionic diffusion processes through the deposit which is present between anodic and cathodic site. Corrosion protection is then provided by the resistance inhibition mechanism. Many authors investigated coated steel substrates which were contaminated before the application of a coating. In a blister the diffusion of cations from the anodic to the cathodic site is found to be rate-controlling at these substrates. This was concluded from a linear relation between the growth rate of a blister and the diffusion coefficient of the cation.
For filiform corrosion on coated steel substrates the growth rate is also related to the cation type. This is clearly shown in figure 3.5\(^8\) and figure 3.10. The latter figure has been determined from measurements of Kaesche\(^{18}\) and Koehler\(^3\). It should be noted that both anion and cation mobility contribute to the calculated diffusion coefficient given in figure 3.10.

![Graph showing the length of a filament versus the diffusion coefficient of the initiating salts solution (0.1 M). Coated steel substrates](image)

**Figure 3.10** The length of a filament versus the diffusion coefficient of the initiating salts solution (0.1 M). Coated steel substrates

The length of the filaments after one month\(^3\) or 27 days\(^{18}\) exposure, was determined from photographs in references 3 and 18. The measurements were performed at a temperature of 25°C\(^{18}\) or 36°C\(^3\) and 85% R.H.. The diffusion coefficient of the solution is defined as the limiting diffusion coefficient of a strong electrolyte at infinite dilution\(^{17}\).

Let us now consider the ionic transport for filiform corrosion on coated aluminium substrates. Radiotracer studies using radioactive chloride (Cl\(^{36}\)) as initiating ion, have shown that most of the ions are carried along in the head of the filiform. Only a few chloride ions will remain in the formed oxide (i.e. the tail)\(^3^{,24}\). There are reasons to believe that at anodic undermining anions diffuse to the anodic site in the edge of a filament. This may be harmful, in particular in case of chloride anions. These anions attack the oxide layer in the front of the filiform head. Anions forms also complex ions with the metal cation. This leads to a more negative equilibrium potential for the anodic reaction and as a consequence this may accelerate the corrosion process.

Finally it should be noted that the coating itself can also supply chloride ions for the electrolyte solution in the filament head. Well-known are vinyl and chlorinated rubber coatings. Hence these coatings are very susceptible for filiform corrosion\(^8\).
3.4 Pretreatments and adhesion studies

The effect of pretreatments of aluminium on the initiation of filiform corrosion has not been well discussed in literature. Therefore in this section only the influence of pretreatments of aluminium on the propagation mechanism is reviewed.

In the past it was suggested that filiform growth is not related to the metallurgical structure of the metal surface\(^2\). A filament has a considerable length in comparison with the size of different types of defects at a metal surface such as intermetallic inclusions and segregations. It is suggested by van Loo that filaments cross these defects without any apparent effect. However filaments do tend to follow the rolling direction of the material\(^1,2,11\) or sand marks with sandblasted substrates\(^2\). This implies that there may be a relation between the growth direction and the morphology of the metal surface.

Metal substrates are pretreated to improve their corrosion properties and the adhesion of a coating. Popular pretreatments are chromate\(^2\) and phosphate conversion layers and anodised layers\(^2\) on aluminium alloys. They reduce in general the incidence of filiform corrosion but they will not completely eliminate it. Cross sections of filaments on coated anodised aluminium substrates showed that the anodised layer was still present in the head and has dissolved in the tail of the filament\(^6\). In chapter 1 it has been discussed that an anodised layer slowly dissolves in alkaline solutions. As a consequence the layer has disappeared in the alkaline tail on aluminium substrate.

Wash-primers permit filiform growth but they retard filiform corrosion significantly\(^2,26\). The presence of inhibitive pigments (chromate inhibitors) in a coating does also not prevent filiform corrosion completely.

As mentioned before pretreatment layers effect in general the adhesion of the organic coating to the substrate. In figures 3.11\(^a\) the area of a filament on sandblasted aluminium is plotted versus the area of a filament on etched aluminium for various coatings. This figure shows that the dimensions of a filament are mainly controlled by the increase of the adhesion strength. As result of sand-blasting or etching a metal surface, a rougher surface is obtained and the adhesion strength of the coating is improved. In section 3.3.3 it was shown that the area of a filament is in some cases proportional to the growth rate of a filament. So the dimensions shown in figure 3.11\(^a\) may reflect filament growth rates.
Figure 3.11: a) The area of a filament on sand-blasted aluminium versus that on etched aluminium for different coatings. b) The detachment pressure of the coating on sand-blasted steel substrates versus the pressure on vapour degreased substrates for different coatings (1). c) Filiform growth rate (volume per day) versus the pressure of initial detachment for different coatings on steel substrates (2).

○ vapour phase degreased and ● sand-blasted substrates.

(1) The pressure is corrected because plastic deformation of the coating during the detachment may occur. Part of the pressure (force) is thus consumed by the plastic deformation, which is assumed to be proportional to the indentation depth (Hardness).

(2) Growth rate is calculated from the given rate, the mean depth of corrosion into the metal which is estimated from a survey given by Ruggen(4), and the width of the filament.

These results are confirmed by experiments of van der Berg et al(12) who applied different types of coatings on sand-blasted and vapour degreased steel
substrates. They measured the adhesion strength by pressing a liquid through a hole in the substrate and determined the pressure of initial detachment. The detachment pressure is related to the adhesion properties of the coating. The pressure for the sand-blasted substrates was about 1.5 times larger than that for the degreased substrates, independent of the coating type (fig. 3.11b). Although the coating type may affect the adhesion strength significantly\textsuperscript{27}, the influence of a pretreatment is much more pronounced. From these results, the growth rate of a filament is determined as a function of the adhesion strength of the coating. It is shown in figure 3.11c. Clearly the growth rate decreases with increasing adhesion strength.

3.5 Conclusions

Filiform corrosion initiates if there is a defect at the substrate-coating interface, salts are present and water can be supplied. The relative humidity at which filiform corrosion begins should depend on the hygroscopic properties of the salts present at the coating defect. In practice however this relation could not be found. Filiform corrosion starts with blister formation and underfilm corrosion. The conditions for a blister to grow in one direction (a filament) are not clear. The main factors and processes for the initiation of filiform corrosion are schematically given in figure 3.12.

The propagation mechanisms are based on anodic undermining for coated aluminium and cathodic delamination for coated steel substrates. For coated steel substrates it is concluded that the permeation properties of the organic coating for oxygen mainly determine the growth rate of blistering and filiform corrosion. For coated aluminium alloys the oxygen permeability of the applied coating is probably not of great importance for the occurrence of filiform corrosion since there are indications that the oxygen supply to the active head takes place through the tail of a filament.

The adhesion properties have a considerable effect on the growth rate of a filament. These are influenced by the coating type and the pretreatment of the substrate. Other factors like ionic transport between anodic and cathodic site, and the water supply of the filament head seem to be of minor importance for the propagation rate.

Ionic transport between the anodic and cathodic site in the head of the filament may slightly determine the filiform growth rate on both aluminium and steel
Figure 3.12  Initiation of filiform corrosion
Propagation of filiform corrosion at coated substrates

- Intact coating
  - Contamination of the coating-substrate interface with salts
  - Coating remains intact during underfilm corrosion process

  oxygen supply through the coating

  Cathodic delamination

  Primary effects:
  - the oxygen permeation properties of the coating
  - the rate of the oxygen reduction reaction at the substrate-coating interface

  Secondary effects:
  - the chemical adhesion properties of the coating
  - ionic conductivity between the anodic and cathodic site
  - the water permeation properties of the coating

- Damaged coating
  - Coating remains intact during underfilm corrosion process

  oxygen supply through the tail of a filament

  Anodic undermining

  Primary effects:
  - the rate of the anodic reaction at the substrate-coating interface

  Secondary effects:
  - the adhesion properties of the coating
  - the formation of complex ions with the metal cation
  - ionic conductivity between the anodic and cathodic site
  - the water permeation properties of the coating

Figure 3.13 Propagation of filiform corrosion
substrates. For coated steel there are reasons to believe that the cation transport to the cathodic edge also determines the filament growth rate. For coated aluminium it is not clear. It is expected that anions moving to the anodic edge in front of the filament provide the ionic current between anodic and cathodic site. They may effect the corrosion rate by formation of complex ions with the metal cation.

Special properties of the coating as their chloride and hydrogen ions content may effect the growth rate considerably.

The water supply to the head is provided by osmosis. In the tail of a filament water is supplied by diffusion through the coating. This only influences the dimensions of a filament and not the growth rate. The water permeation properties of a coating are thus of minor importance for the propagation mechanism. In figure 3.13 the propagation of filiform corrosion is schematically summarised.

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III CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS
4.1 Introduction
The high corrosion resistance of aluminium alloys is attributed to the formation of a highly protective oxide film which separates the bare metal from the corrosive environment. This passive film on aluminium can be formed directly in humid air or at exposure to an aqueous electrolyte solution. Due to the presence of a passive film, the metal protects itself against further attack.

The corrosion resistance of aluminium alloys is determined by several factors, which are effecting the protective properties of the passive layer. Alloying elements may considerably influence the corrosion resistance of an aluminium alloy. In general, the higher the purity of aluminium is, the greater is its corrosion resistance. The corrosion rate of nearly pure aluminium for example increases appreciably as the purity drops from 99.998% to 99.98%. This is caused by the fact that intermetallic phases can be formed which may effect the local properties of the passive layer and eventually cause weak spots in the film. In addition the electrode potential of these phases differs often considerably from that of the aluminium matrix. As a consequence contact corrosion between intermetallic phases and the aluminium matrix may occur leading to various local corrosion phenomena.

The corrosion resistance of aluminium depends also on the pH of the solution. Aluminium remains passive in aqueous solutions across a pH range of approximately 4 to 8.5. Outside this range aluminium oxide dissolves chemically as aluminium ions (Al^{3+}) in acid solutions and as aluminate ions (AlO_2^-) in alkaline solutions. Even in these solutions, a passive layer of aluminium oxide is assumed to be present.

The passive behaviour of aluminium is well recognisable in a polarisation curve of the metal. When recording such a curve, the current density is measured as a function of the electrode-potential of a metal, often starting at the open circuit potential (OCP) and slowly scanning into the direction of more positive potentials. For a freely corroding system the OCP is also called the corrosion potential.
Polarisation curves of aluminium in alkaline, neutral and acid solutions were already shown in figure 2.3 in chapter 2. It was mentioned that the curves of aluminium at anodic potentials considerably deviate from the normal Evans diagram due to the presence of a passive layer on aluminium. The very low passive current density $i_{\text{pas}}$, even in acid solutions, is the current to maintain the passive layer while slowly dissolving chemically. In many different solutions, aluminium is normally passive. This is due to the fact that aluminium is very unnnoble ($E_{\text{Al/AI}_3^+}$ is very negative). Therefore aluminium is spontaneously passivated by either the oxygen reduction reaction or, when oxygen is absent, by the reduction reaction of water. A damaged passive film is thus self-repairing.

In summary, it can be said that the corrosion protection of aluminium alloys in all environments is provided by the well-adherent and non-porous oxide layer. To obtain more insight into the formation of such a passive layer on aluminium, pure aluminium has been examined at several anodic potentials. The results of these investigations are discussed in this chapter.

The content of this chapter is as follows. In section 4.2 the experimental conditions of the polarisation and impedance measurements are summarised. Also a brief comment is given on the interpretation of impedance measurements. In section 4.3 the general passive behaviour of aluminium, reflected in polarisation curves, is discussed. In section 4.4 literature is reviewed, concerning models that describe the passive film growth under potential control. A promising model that can account for layer growth is the point defect model (P.D.M.). This model is discussed in section 4.5 and applied to our measured polarisation curves in section 4.6. In section 4.7 a revised model is presented and the corresponding impedance expression is derived and applied to our impedance data. Finally in section 4.8 some conclusions are given.

4.2 Experimental
4.2.1 Experimental conditions

Pure aluminium cylinders (99.995%, Johnson Matthey Ltd) with a diameter of 0.6 cm were first covered with a two component resin (Metacoat F495, Sikkens NL) and then embedded in another epoxy resin (Epikote 828 Shell and Loromin C260 Hardener, BASF). Only one side of the embedded aluminium cylinder was exposed to the electrolyte. The embedded electrodes were abraded (grit P600), polished (1μm), ultrasonically cleaned and finally rinsed with alcohol. The
electrodes were mounted in a rotating rotor cell. This cell has been especially constructed to obtain the same characteristics as a rotating disk electrode. A detailed description of the cell is given elsewhere\textsuperscript{3}.

The electrolyte solution was de-aerated with high purity nitrogen gas. The electrolyte solutions used in the experiments were

- 0.1 M HNO\textsubscript{3} solution (pH = 1.2)
- 0.1 M and 1 M H\textsubscript{2}SO\textsubscript{4}, pH respectively 1.2 and 0.3.
- 1 M Na\textsubscript{2}SO\textsubscript{4} (H\textsubscript{2}SO\textsubscript{4}) solutions with a pH of 2.2, 3, 4.2.
- 0.1 M and 1 M Na\textsubscript{2}SO\textsubscript{4} solution (pH=5.7),
- 0.1 M K\textsubscript{2}SO\textsubscript{4} solution (pH=5.7),
- 0.1 M and 1 M NaNO\textsubscript{3} solution (pH=5.7)
- 1 M CH\textsubscript{3}COONa /CH\textsubscript{3}COOH buffer (pH=6.0),
- 0.1 M and 1 M CH\textsubscript{3}COONa solutions,

These solutions were prepared from analytical grade (Merck) salts and de-ionised water. All potentials were measured versus a saturated Hg/HgSO\textsubscript{4} (SSE) electrode (660 mV (pH=0.3, T=293K) vs. NHE) and the potentials in this chapter are given with respect to this electrode.

Before starting an impedance measurement, the electrode was left at open circuit for several hours to obtain a stable corrosion potential and then polarised at a chosen anodic potential. During the measurements the solution was mechanically stirred (1.8 rps) and purged with nitrogen. The impedance measurements were recorded when the current fluctuations were less than 2.5 % of the total current during 1 minute. The amplitude of the perturbation was 5 mV and the frequency range was from 99 kHz to 1 mHz. To check whether the system is stable, the frequency range between 1 and 0.1 Hz was measured twice. All measurements were performed in a Faradaic cage. A Schlumberger Electrochemical Interface, model 1286, and a Schlumberger Frequency Response Analyser, model 1255, were used for the impedance measurements. The polarisation curves were recorded using a EG&G PAR 273 potentiostat. The electrode potential was scanned from -100 mV to 1500 mV versus OCP at a scan rate of 0.1 mV/s. All polarisation curves were recorded at least twice and at least three impedance measurements were performed at a given potential.
4.2.2 Interpretation of impedance measurements

Impedance measurements are very popular in corrosion research. This is due to the fact that different processes are reflected in different frequency ranges and as a consequence reaction mechanisms can be revealed. However, interpretation is often difficult because the frequency ranges for different processes may overlap.

There are in general two different methods to interpret the measured impedance data\(^3,4,5\). The first method uses electrical equivalent circuits. The circuit should have a similar impedance characteristic in the frequency range measured as the measured impedance data. Alternatively a transfer function can be calculated, i.e. a theoretical impedance expression based on an assumed physical model. The latter method is a more fundamental approach but often corrosion systems are too complicated to arrive at useful transfer functions. In that case the impedance data are in general analysed according to the first method. In this chapter the impedance measurements are analysed by the calculation of a transfer function. An equivalent circuit can be useful to obtain the parameters from the transfer function (the model). So, an equivalent circuit is fitted to the measurement data. The program Equivcrt, was used to fit the equivalent circuit. The fit is here based on a non-least squared fitting procedure. A similar approach was recently followed by Dobbelaar\(^3\).

<table>
<thead>
<tr>
<th>element</th>
<th>symbol</th>
<th>impedance expression, (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>resistance</td>
<td>R</td>
<td>(R)</td>
</tr>
<tr>
<td>capacitor</td>
<td>C</td>
<td>(\frac{1}{j\omega C})</td>
</tr>
<tr>
<td>Inductance</td>
<td>L</td>
<td>(j\omega L)</td>
</tr>
<tr>
<td>Warburg</td>
<td>(W)</td>
<td>(Y_0(j\omega)^{-1/2}) with (\sigma = \left(\frac{Y_0}{\sqrt{2}}\right)^{-1})</td>
</tr>
<tr>
<td>O.F.D.I.</td>
<td>(O)</td>
<td>(\tanh\left[\frac{B\sqrt{j\omega}}{Y_0\sqrt{j\omega}}\right]) with (B = \frac{\delta_n}{\sqrt{D}})</td>
</tr>
<tr>
<td>B.F.D.I.</td>
<td>(B)</td>
<td>(\coth\left[\frac{B\sqrt{j\omega}}{Y_0\sqrt{j\omega}}\right]) with (B = \frac{\delta_n}{\sqrt{D}})</td>
</tr>
</tbody>
</table>

Table 4.1 Some electrochemical impedance elements \(^4\)

\(^{1}\) \(W\): Warburg Element, \(^{2}\) O.F.D.I.: Open Finite length Diffusion Impedance, \(^{3}\) B.F.D.I.: Bounded Finite length Diffusion Impedance. \(\delta_n\) is Nernst diffusion layer thickness; \(D\) is diffusion coefficient of the electro-active species; \(\sigma\) is Warburg coefficient

An equivalent circuit is in general constructed from commonly encountered elements in network theory such as resistors, capacitors and inductances. These
elements can represent certain physical or chemical processes. Examples are the charge transfer resistance and the double layer capacitance. Adsorbed intermediates, involved in an electrochemical reaction, are often represented as an inductor (L). Besides these elements, also other elements are encountered in electrochemistry. These are specifically related to physical or chemical phenomena in reaction mechanisms. For example, diffusion processes can be described by a Warburg element (W) and a finite length impedance element O. In table 4.1 the elements, relevant for this thesis, are given. For other elements used in equivalent circuits one is referred to literature\(^3\text{-}^5\).

The impedance of a circuit, \(Z\), can be derived from the impedance expressions of the individual elements according to the following rules: 1) The impedance of a series combination of elements is the sum of the impedances. 2) The admittance, defined as \(Y=1/Z\), of a parallel combination of elements is the sum of the admittances of the elements.

The procedures for construction of a circuit have been described in detail by Geenen\(^9\). Recently these were discussed in references 10 and 11. In this section the procedures are briefly pointed out. The circuit is often based on a qualitative model which has been derived from other research results. The number of time constants should be as low as possible without loosing significant fitting accuracy. The circuit is fitted to the measured impedance data. The quality of the fit is reflected in some factors which will be discussed furtheron in this section. It determines whether the circuit (and hence the model) should be excepted or rejected. A second check for the validity of a model is the logical variation of the values of the components of the circuit with experimentally influenced parameters as exposure time and electrode potential.

The quality of a fit is reflected in the values of the following parameters, obtained after the fitting procedure: the relative error in the value of the components of the equivalent circuit, \(\chi^2\), the error plot and the table of the correlation factors\(^12\). The parameter \(\chi^2\) is an overall indication for the quality of the fit. It indicates the differences between the fit value and the measured value of individual frequency points, summarised quadratically over all frequency points. The error plot shows the scaled individual fit errors as a function of the frequency. The criteria for a good fit are a bit arbitrary. The relative errors in the values for the components should be small and equally distributed over the components in
the circuit. For values of $\chi^2$ smaller than $10^{-4}$, the fit is considered good. The errors of the individual data points in the error plot should be less than about 5%. Moreover the distribution of the errors over the full frequency range should be random and not follow a recognisable sinus wave. This may represent an extra time constant. The fit program also provides a table of correlation factors, showing a possible mutual dependence between the elements of the equivalent circuit. When the correlation factor of an element with another is larger than 0.92, the value is not reliable because these are coupled. All impedance data in this thesis were fitted according to these rules.

4.3 Passive film growth under potential control
4.3.1 Structure and composition of the passive film
The structure and composition of anodic oxide films on aluminium are complicated. The film has a multiple layer structure. An anodised layer on aluminium consists of a non-porous barrier layer (several nanometers) and a porous layer of several micrometers thickness. A schematical representation is shown in figure 4.1.

![Figure 4.1 Schematic representation of the oxide layer on anodised aluminium](image)

The upper porous layer may consist of different oxides or hydroxides as e.g. Al(OH)$_3$, AlOOH or $\gamma$-Al$_2$O$_3$ and $\gamma'$-Al$_2$O$_3$ and is usually amorphous$^2$. Anions from the electrolyte solution can be incorporated in the film during oxide growth. In particular phosphate ions are easily incorporated$^2$. Anions are mainly present in the outer layer of the film. The penetration depth depends strongly on the anion type. Penetration depth of 40% of the total film thickness was found for borate
ions and 70% for phosphate anions\textsuperscript{1}. The incorporation of these anions in the oxide may considerably effect the properties of the oxide as for example the oxygen ion and aluminium ion mobility, the overall electrical conductivity, the dielectric properties and the film growth rate.

As a result of deprotonation of the aluminium hydroxides in the porous layer, the morphology of the film can change to a more compact oxide, consisting of hydrated aluminium oxide.

The thickness of the barrier layer on aluminium, formed in humid atmosphere, is varying between 2 and 5 nm\textsuperscript{2}. The film thickness increases during anodising aluminium with about 0.8 to 2 nm/V\textsuperscript{1,2,13}. For our measurements, the thickness of the passive film is probably not larger than 2 to 5 nm.

\textbf{4.3.2 Models for passive film growth}

Despite the multiple layer structure of the passive layer on aluminium, the oxide layer is considered to be homogeneous and not porous in studies towards modelling of the passive film growth. It is often assumed that the upper porous layer is very permeable for water and aluminium ions. As a consequence the electrochemical reaction takes place at the interface of the barrier layer and the porous layer c.q. electrolyte solution. Also in this chapter the O/S interface is considered to be located at this interface.

Models, describing the passive film growth, should incorporate processes in the passive film and at the interfaces. Electrochemical reactions take place at the interfaces of the passive film. Aluminium is oxidised at the metal-oxide (M/O) interface, as for metal dissolution in aqueous solutions, forming Al\textsuperscript{3+} ions. An electrochemical double layer should be established at this interface with aluminium oxide as a solid electrolyte. It is often assumed that the diffuse double layer thickness is small at this interface and hence the double layer is determined by the Helmholtz layer\textsuperscript{1}.

At the oxide-solution (O/S) interface, an oxygen ion must be taken up in the oxide\textsuperscript{14}. Oxygen ions can be formed according to the reaction sequence 4.1 to 4.3, as published in literature by Valand and Heusler\textsuperscript{15}:  

\[ \text{4.1: } \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{2e}^- \]  
\[ \text{4.2: } \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 \]  
\[ \text{4.3: } \frac{1}{2}\text{O}_2 + \text{2H}^+ + \text{2e}^- \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{H}_2\text{O} \rightleftharpoons \text{OH}^-_{\text{ad}} + \text{H}^+ \]  
(4.1)

\[ \text{OH}^-_{\text{ad}} \rightleftharpoons \text{O}^{2-}_{\text{ad}} + \text{H}^+ \]  
(4.2)

\[ \text{O}^{2-}_{\text{ad}} \rightarrow \text{O}^{2-}_{\text{ox}} \]  
(4.3)

The last step, eq. 4.3, is the rate-determining step in the overall reaction. It should be noted that in this mechanism the adsorbed oxygen ion diffuses over the O/S interface before it is incorporated in the oxide.

Both aluminium and oxygen ions, but also other species (impurities), will move across the oxide. Aluminium ions will move to the O/S interface where they dissolve. Oxygen ions however, move from the O/S to the M/O interface. In particular a thick aluminium oxide layer behaves as an isolator with a dielectric constant varying between 7.5 and 12. When aluminium is polarised anodically (e.g. 1 V), the electric field strength in a passive layer (10 nm thick) is in the order of $10^6$ V/cm. Therefore the driving force for ionic transport through the oxide is migration. From experimental results the field strengths are calculated and are found to be in the order of $10^6$ to $10^7$ V/cm \(^1,2\). Scientists of the Chalk-River Nuclear Laboratories\(^{16-23,50-53}\) did Nuclear Reaction Analysis studies to identify mobile species in anodic films for a large number of metals (Al, Nb, W, Ta, Hf, Si, Zr). The transport numbers of the mobile species were determined, indicating the relative contribution of mobile species to the film growth. The results showed for anodised aluminium that the ionic transport number of aluminium ions is about 0.4 and that of oxygen ions about 0.6. So both aluminium cations as oxygen anions contribute to the film growth. It should be mentioned that these results suggest that the transport paths of aluminium and oxygen ions are different. Otherwise oxide is formed in the passive layer itself.

A number of models for passive film growth was proposed by Verwey, Mott-Cabrera, Vermilyea-Vetter, Sato-Cohen, Fehler-Mott and Chao-Lin-Macdonald. These models are extensively reviewed in references 1, 2 and 24; so only a brief discussion is given in this section.

Basically, all models assume that ionic species migrate through the film as a result of a constant high electric field. The assumed main transport mode across the oxide is either through oxygen anions (Fehler-Mott, Sato-Cohen, Chao-Lin-
Macdonald) or aluminium cations (Verwey, Vermilyea-Vetter, Mott-Cabrera). Another point is the rate-determining step. In the Vermilyea-Vetter and the Verwey model the cation transport in the oxide is rate-controlling. Other authors assume that the overall reaction rate is controlled by either the cation transfer reaction at the M/O interface (Mott-Cabrera\textsuperscript{47-49}) or the anion transfer reaction at the O/S interface (Sato-Cohen, Fehler-Mott). In the latter case the authors used the so-called "place-exchange" mechanism to explain their results. According to this model, a layer of oxygen species is adsorbed onto the oxide surface which then collectively exchange places with the underlying metal cations layer. This process continues and consequently the film will grow. In the point defect model of Chao, Lin and Macdonald, the layer may be a cation conductor or an anion conductor, or both, depending on the kinetics at the interfaces\textsuperscript{25,26}.

Let us now briefly evaluate the models. Various parameters introduced in the models of Verwey, Mott-Cabrera, Vermilyea-Vetter, Sato-Cohen and Fehler-Mott, are not easily brought in relation with data obtained from electrochemical methods. Some examples of these parameters are a jump-distance for the migrating ions, a vibrational frequency of the lattice ions, and the number of mobile ions per surface area. The point defect model of Chao-Lin-Macdonald however, is promising since both interfacial processes and transport phenomena are taken into account. Both are directly measurable with electrochemical techniques. In addition it should be noted that this model is also able to describe the formation of a porous oxide layer\textsuperscript{27}. In section 4.4 this point defect model will be further discussed.

4.3.3 Results of impedance measurements

Various "charge" related processes can be separately observed by measuring the impedance of passive aluminium. As discussed in section 4.2.2, the time constants, associated with the different processes, may considerably differ and therefore dominate the impedance in different frequency ranges. Hence the mechanism of film growth can in principle be revealed. For this reason impedance measurements are intensively used in corrosion research. In this section the results of anodic film growth on aluminium, reported in literature, are reviewed and compared with new own results.
A Nyquist plot of passive aluminium under anodic potential control, typical for electrolyte solutions as sulphuric acid, hydrochloric acid, sodium sulphate and phosphate solutions, phosphoric and acetic acid solutions, is shown in figure 4.2. At first sight at least three time constants are observed: 1) a time constant at high frequencies (capacitive loop), 2) a time constant at intermediate frequencies (inductive loop) and 3) a time constant at low frequencies. It should be noted that the shape of the latter time constant is not very reproducible.

![Figure 4.2](image)

**Figure 4.2** Typical Nyquist plot of passive aluminium under potential control. Experimental conditions: 1 M sulphuric acid solution, potential -800 mV (SSE).

Similar impedance plots were reported in literature\textsuperscript{13,28-32}. There is however no consensus on the origin of the different time constants. Brett\textsuperscript{29-31} attributed the time constant at high frequencies to the interfacial reactions, in particular the metal oxidation reaction at the M/O interface. He suggested that aluminium is oxidised to Al\textsuperscript{3+} intermediates which are subsequently oxidised to Al\textsuperscript{4+} ions. Bessone et al\textsuperscript{13} however reported that this time constant could be ascribed to the oxide layer on aluminium. The reason is that he found a linear relation between the inverse of the capacitance and the potential. This result was confirmed by Wijenberg et al\textsuperscript{28}.

The origin of the inductive loop at intermediate frequencies is not quite clear. Burnstein\textsuperscript{6-8} performed single frequency impedance measurements during the repassivation of a damaged passive layer. To this end, a guillotine equipment was specially developed to destroy the passive layer locally in situ. The overall impedance plot was constructed by performing many single frequency impedance measurements. In Burnstein's measurements no inductive loop in the impedance plot was observed. This may indicate that the inductive loop is closely related to
the existence of a passive film on aluminium. Wijenberget al.\textsuperscript{28} suggested that this inductive time constant is the result of a rearrangement of surface charge at the M/O interface.

As mentioned before the shape of the third time constant at low frequencies is not reproducible. Brett\textsuperscript{29-31} found a similar shape for the impedance at low frequencies as in figure 4.3 and attributed this time constant to the reaction at the O/S interface.

No inductive loop was obtained in some electrolyte solutions, e.g. in potassium sulphate, sodium nitrate, and nitric acid solutions. Figure 4.3 shows the characteristic Nyquist plot of aluminium for these solutions. The capacitive time constant at low frequencies changes into a Warburg impedance response at more positive anodic potentials. Such a behaviour was also reported by KrishnquaKumar and Szklarska-Smialowska\textsuperscript{30} for some impedance measurements in chloride solutions. They suggested that the Warburg impedance is due to ionic diffusion through the barrier oxide layer.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Nyquist_plot.png}
\caption{A typical Nyquist plot of aluminium in a 0.1 M sodium nitrate solution. Potential -600 mV.}
\end{figure}

The origin of the different behaviour of passive aluminium (compare fig. 4.2 and 4.3) in different electrolytes is still unclear. It may be caused by specific adsorption of ions from the electrolyte solution, in particular anions. In addition anions can also be incorporated into the (porous) oxide lattice as was mentioned in section 4.3.1. The mechanism is therefore rather complicated and as a consequence the measured impedance data.
From the discussion above it became clear that there is no consensus in literature on the interpretation of the different time constants. This is mainly caused by the fact that there is no model available which can be used for a fit to measured impedance data. Recently Bessone et al.\(^{32}\) suggested that the defect chemistry should be used interpreting impedance data of passive layers on aluminium. Both electrochemical reaction at the interfaces and ionic migration through the oxide can then be incorporated into a model for passive film growth. As suggested before, the Point Defect Model (P.D.M.) proposed by Chao, Lin and Macdonald\(^{24-27,34-40}\) is appropriate for this.

4.4 The Point Defect Model
4.4.1 Reaction mechanism

The point defect model was proposed by Chao, Lin and Macdonald in the eighties\(^{24-27,34-40}\). The model is based on the oxidation theory of Wagner, which was originally derived for high temperature oxidation. Macdonald et al. applied this theory on low temperature oxidation of metals in aqueous electrolyte solutions under potential control. In this section the model is discussed in more detail.

As usual in studies of passive film growth, Macdonald considered also only the barrier layer. He assumed that the porous upper layer is easily permeable for water. Hence the oxide-solution interface is positioned at the interface between the barrier layer and the porous top layer.

The point defect model describes the film growth of the barrier layer. As discussed before it is assumed that its structure is very compact, consisting of hydrated aluminium oxide. Macdonald also assumes that the oxide has a defective crystalline structure. Only single vacancies (point defects) are considered, excluding any higher dimensional defects. Anion vacancies (i.e. missing oxygen anions) have an effectively positive charge and cation vacancies (i.e. missing aluminium cations) an effectively negative charge. They will move across the passive film when an external electric field is applied at polarisation.

According to the point defect model of Macdonald the following two reactions take place at the metal-oxide interface (M/O):

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\[ \text{Al} + V_{\text{Al}}^{3'} \xrightarrow{k_1} \text{Al}_{\text{AL}} + 3e^- \] (4.4)

\[ \text{Al} \xrightarrow{k_2} \text{Al}_{\text{AL}} + \frac{3}{2} V_{\text{O}} + 3e^- \] (4.5)

and at the oxide-solution interface (O/S):

\[ \text{Al}_{\text{AL}} \xrightarrow{k_3} \text{Al}^{3+} + V_{\text{Al}}^{3'} \] (4.6)

\[ \text{H}_2\text{O} + V_{\text{O}} \xrightarrow{k_4} \text{O}_2 + 2H^+ \] (4.7)

Besides reactions 4.4 to 4.7 the oxide layer dissolves chemically, e.g. at a kink site:

\[ \left[ \text{Al}_{\text{AL}} + \frac{3}{2} \text{O}_2 \right] + 3H^+ \xrightarrow{k_5} \text{Al}^{3+} + \frac{3}{2} \text{H}_2\text{O} \] (4.8)

where the entity contained within the squared brackets represents the oxide lattice. The reactions 4.4 to 4.8 are also indicated in figure 4.4. Reactions 4.4, 4.6 and 4.7 are lattice conservative reactions which means that vacancies are formed or filled. However reaction 4.5 and 4.8 are not lattice conservative. They will contribute to the oxide growth and break down.

The electrochemical nature of reactions 4.4 and 4.5 is obvious because electrons are explicitly present in the reactions. This is not the case for reactions 4.6 and 4.7. Let us thus consider reaction 4.6 and 4.7 in more detail.

Reaction 4.6 should in principle formally be written as:

\[ \text{Al}_{\text{AL}} \xrightarrow{k_3} \text{Al}^{3+}_{\text{aq}} + 3e^- + \left[ 3h_{\text{ox}}^* + V_{\text{Al}}^{3'}(\text{ox}) \right] \] (4.9)

where \( h_{\text{ox}}^* \) is a hole in the oxide compensating the electric charge in the oxide and \( e^- \) the electrons explicitly resulting from the formation of \( \text{Al}^{3+}_{\text{aq}} \) from neutral \( \text{Al}_2\text{O}_3 \) (charge transfer). Likewise, reaction 4.7 is the result of the chemical dissociation of water at the O/S interface and an oxide formation reaction:

\[ \text{H}_2\text{O} \xrightarrow{k_{-7},k_7} \text{O}^{2-}_{\text{aq}} + 2\text{H}^+ \] (4.10)
\[ V_0 + O_{ad}^{2-} \xrightarrow{k_8} O_0 \]  \hspace{1cm} (4.11)

Reaction 4.11 should in principle be written as

\[ V_O^{\text{ox}} + O_{ad}^{2-}^{\text{aq}} \xrightarrow{k_8} \left[ O_0^{\text{ox}} + 2h_{ox}^* \right] + 2e^- \]  \hspace{1cm} (4.12)

where charge transfer is now again explicitly visible. Reactions 4.9 and 4.12 are obviously also electrochemical reactions.

\[ \text{Metal} \quad \text{Barrier layer} \quad \text{Precipitated outer layer, solution} \]

\[ \begin{align*}
V_{\text{Al}}^{3'} & \text{ } V_{\text{Al}}^- \text{ } V_{\text{O}}^- \\
\text{Al} + V_{\text{Al}}^{3'} & \rightarrow \text{Al}_{\text{Al}} + 3e^- \\
\text{Al} & \rightarrow \text{Al}_{\text{Al}} + \frac{3}{2}V_{\text{O}} + 3e^- \\
H_2O + V_{\text{O}}^- & \rightarrow O_0 + 2H^+ \\
\left[ \text{Al}_{\text{Al}} + \frac{3}{2}O_0 \right] + 3H^+ & \rightarrow \text{Al}^{3+} + \frac{3}{2}H_2O \\
\end{align*} \]

**Figure 4.4**  Physico-chemical processes, occurring within the barrier layer according to Macdonalds Point Defect Model (P.D.M.)\textsuperscript{24-27,34-40}. Al is a aluminium atom, Al\textsubscript{Al} is a aluminium cation at a cation site of the oxide, O\textsubscript{O} is an oxygen ion at an anion site, V\textsuperscript{3'}\textsubscript{Al} is a cation vacancy, V\textsuperscript{-}\textsubscript{O} is an anion vacancy. The fluxes of cation and anion vacancies during film growth are in the directions indicated.

It is apparent that the oxygen ion vacancies are produced at the metal-oxide interface (eq. 4.5) but are consumed at the oxide-solution interface (eq. 4.7). As a
result, oxygen ion vacancies diffuse from the metal-oxide to the oxide-solution interface. Likewise, aluminium ion vacancies are produced at the oxide-solution interface (eq. 4.6), but are consumed at the metal-oxide interface (eq. 4.4). Consequently the aluminium ion vacancies diffuse from the O/S to the M/O interface. Another implication of the point defect model is that the fluxes of aluminium and oxygen ion vacancies across the film are mutually independent.

It is clear from the net transport of oxygen ion vacancies, eqs. 4.5 and 4.7, that the oxygen ion vacancies transport results in oxide growth at the metal-oxide interface (eq. 4.5). Similarly (eqs. 4.4 and 4.6), the cation transport (aluminium cations vacancies) across the oxide results only in dissolution of aluminium ions at the oxide-solution interface. The fact that only the oxygen anion transport contributes to the film growth conflicts with the results of measurements performed at the Chalk-River Nuclear Laboratories\textsuperscript{16-23,50-53} where mobile species in anodic films for a large number of metals (Al, Nb, W, Ta, Hf, Si, Zr) were identified. As discussed before the transport number of oxygen ions in an anodised layer on aluminium is only about 0.6. In other semi-conductors as Si and Zr it is found that the transport number of the oxygen ion is very closely to unity. In all cases the major contribution to the film growth is provided by the oxygen anion. For this reason Macdonald neglected the following reaction, which also should occur at the oxide-solution interface when the defect chemistry is applied:

\[ \text{H}_2\text{O} \xrightarrow{k_{10}} \text{O}_6 + \frac{2}{3} \text{V}^{3+}_\text{Al} + 2\text{H}^+ \quad (4.13) \]

By incorporating this reaction into the reaction mechanism the film growth also takes place at the oxide-solution interface as result of cation vacancies transport across the film.

4.4.2 Structure of the oxide film on aluminium and the PDM

Recently Macdonald extended his model to describe also the porous structure of the oxide film on aluminium\textsuperscript{27}. In this section a brief discussion of this aspect of the point defect model is given.

Macdonald\textsuperscript{27} suggested that the porous oxide layer is formed due to condensation of vacancies at the metal-oxide interface (fig. 4.5\textsuperscript{a}). Aluminium ion
vacancies may condensate at the M/O interface, when reaction 4.4 is not able to
annihilate the vacancies which were produced according to reaction 4.6. Another
possibility is associated with the vacancies which are left in the metal surface
layer when aluminium atoms transfer from the metal substrate to the oxide.
Reaction 4.4 may also be written as

\[ \text{Al} + V_{\text{Al}}^{3+} \rightarrow \text{Al}_{\text{AL}} + V_{\text{AL}} + 3e^- \quad (4.14) \]

where \( V_{\text{AL}} \) is a vacancy in the metal surface layer.

When the rate of this reaction is so fast that the vacancies in the metal can not
diffuse fast enough into the metal, the left vacancies may condensate at the
interface (fig. 4.5a). Local decohesion of the oxide film from the metal at the
metal-oxide interface will then occur (fig. 4.5b). Since during film growth, the M/O
interface moves into the metal, the growth of the oxide layer is inhibited at voids.
In neighbouring regions it continues to grow as is depicted in figure 4.5c. Thus,
the vacancy condensates (voids) coincide with protrusions of the metal into the
oxide layer. The protrusion formation process has the effect of undercutting the
void with the consequence that the void becomes detached from the apex of the
protrusion (fig. 4.5d). Then a new void can nucleate on the apex. When the
process (nucleation \( \rightarrow \) growth \( \rightarrow \) detachment) is repeated several times, a porous
structure of the oxide layer will result (fig. 4.5e).

The locations where vacancies may easily condensate are the regions in the
barrier layer that support the greatest flux of aluminium vacancies since the
coordination number of the ions of the oxide lattice is relatively small. Clearly,
candidates are defects as e.g. grain boundaries. The rate of ejection of aluminium
ions at the O/S interface is determined by the externally applied potential. When
the potential is more positive, the ejection of aluminium ions from the oxide lattice
increases. Macdonald assumed that externally applied potential influences only
the O/S interfacial potential. The M/O interfacial potential is assumed to be
constant. Consequently the consumption rate of aluminium vacancies at the M/O
interface is constant whereas the production rate at the O/S interface varies
considerably with the applied potential. This may result in a surplus of vacancies
at the M/O interface which may condensate (formation of voids).
Figure 4.5 The process of the formation of a porous anodic film on aluminium, proposed by Macdonald.

It should be noted that the formation of voids in anodic oxide films on aluminium has been reported by several authors. These voids were observed at the protrusions of the aluminium substrate into the oxide film. The average diameter of the voids varies between 25 nm when the oxide layer is formed at 40 V, to about 50 to 100 nm at 160 V.
Macdonald mentioned that many details undoubtedly have to be resolved, but that
the mechanism outlined before can account for the void formation in anodic oxide
barrier layers on aluminium.

4.4.3 Main points of interest in the PDM
The following five main points of the point defect model are now discussed in
more detail.

- Macdonald assumed that the oxide can be regarded as a "incipient semi-
  conductor". Hence the electrons and the electron holes in the film are in their
  equilibrium states, and the electrochemical reactions involving electrons or
  electron holes are rate controlled at either the metal-oxide or the oxide-solution
  interfaces. On the other hand, the rate of the reactions at the interfaces depends
  on the transport of aluminium and oxygen ion vacancies across the film.
  It should be noted that aluminium is often slightly contaminated by small
  concentrations of impurities. This inevitably results to a semi-conductor behaviour
  of the oxide. More important is probably the fact that an oxide may obtain some
  semi-conductor behaviour when anions from the electrolyte solution are
  incorporated in the oxide\(^1,2\). Alternatively electrons can tunnel through thin
  passive films of several nanometers thickness\(^38\).

- The field strength in a passive layer is in principle a function of the chemical and
  electric characteristics of the film. Macdonald et al assumed that a high field
  strength of \(10^6\) V/cm, exists in the passive film. Moreover it was assumed that the
  field strength is constant and not potential dependent, even when the oxide film
  obtains semi-conductor behaviour or when the concentration of alien ionic
  species, present in the film, is relatively large. This assumption is contrary to the
  common assumption that a passive film, in particular on aluminium, may be
  modelled as a dielectric capacitor. If a passive film does behave like a capacitor,
  the field strength in the film has to vary with the applied potential. Macdonald
  evaluated the values, found in literature, of the electrical field strength for different
  metals\(^16\). It is striking that the field strength, measured by ellipsometric and
  coulometric techniques, is rather constant and slightly dependent on the pH of the
  solution. This even holds for aluminium where it seems to be reasonable due to
  the extrinsic semi-conductive behaviour of the oxide film.

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• Figure 4.6 shows schematically the potential-position relationships across the metal-oxide-solution system. The parameters $\phi_{mo}$, $\phi_{os}$, $\phi_{ref}$ represent the potential drop at the M/O, O/S and the solution-reference electrode interfaces. The parameter $\phi_f$ is the potential drop in the oxide layer and $E$ the externally applied potential. The potential drop in the electrolyte solution is neglected.

![Diagram of potential relationships](image)

*Figure 4.6 The potential-position relation for a metal-oxide-solution system*

From figure 4.6 we obtain the following relation:

$$E + \phi_{ref} = \phi_{mo} + \phi_f + \phi_{os}$$

(4.15)

The potential drop at the oxide-solution interface is assumed to be a function of the applied potential and the pH of the solution, but independent of the anodic film thickness. Accordingly, we may express $\phi_{os}$ as:

$$\phi_{os} = \alpha E + \gamma p H + \phi_{os}^0$$

(4.16)

where $\alpha$ and $\gamma$ are constants and $\phi_{os}^0$ is the potential drop at the O/S interface at pH=0 and when no external potential is applied. The extend at which the O/S interface is polarised by the externally applied potential $E$, is given by the parameter $\alpha$. The potential- and pH- dependence of $\phi_{os}$ seems to be justified since the oxide-solution interface is polarisable. Macdonald calculated the expression for $\phi_{mo}$ by combining eqs. 4.15 and 4.16:

$$\phi_{mo} = (1-\alpha)E - \gamma p H - \phi_{os}^0 + \phi_{ref} - \phi_f$$

(4.17)
The remaining fraction \((1-\alpha)\) of \(E\) contributes to the polarisation of the \(M/O\) interface since a constant potential drop is assumed to exist over the oxide film. The electric field strength \(\varepsilon\) in the film is assumed to be constant which results in a very simple expression for \(\phi_f\):

\[
\phi_f = \varepsilon L
\]  

(4.18)

in which \(L\) is the film thickness. Although eq. 4.17 is formally correct, the equation suggests that the thickness of the oxide film is a constant. However, the thickness is not constant but a function of the externally applied potential \(E\). In appendix 1 the thickness of the oxide film is calculated for steady state conditions. This means that the chemical dissolution rate, eq. 4.8, is equal to the rate of the passive film growth, eq. 4.5. It is shown that the thickness of the passive film increases linearly with the applied potential, according to the following equation:

\[
L = \frac{(1-\alpha)}{\varepsilon}(E-E^*)
\]  

(4.19)

where \(E^*\) is a constant (see appendix 1). It is clear from eqs. 4.18 and 4.19 that the potential drop in the oxide film \(\phi_f\) is proportional to \((1-\alpha)E\). Since the fraction \(\alpha\) of the applied potential \(E\) is applied on the \(O/S\) interface, the remaining fraction \((1-\alpha)\) of \(E\) is due to the potential drop in the oxide film. The potential drop at the \(M/O\) interface must therefore be constant and could not be dependent on the applied potential \(E\). Several authors stated that there is a constant potential drop at the \(M/O\) interface\(^{14,27}\) which confirms the constant potential drop according to Macdonald's point defect model. In the next point of interest the constant potential drop at the \(M/O\) interface is derived.

- It is noted that the rates of the electrochemical reactions at both interfaces depend exponentially on the overpotential, \(\eta\), according to Tafel's law:

\[
k_i = k_i^0 \exp(b_i \eta)
\]  

(4.20)

Where \(\eta\) is the overpotential at an interface, defined as:

\[
\eta = \phi_{os} - \phi_{os}^*
\]  

(4.21)
\[ \eta = \phi_{m0} - \phi_{o0} \] (4.22)

and \( b \) is the Tafel slope, and finally \( k_i^o \) is the reaction rate at \( \eta = 0 \). \( \phi_{m0} \) is the constant potential drop at the M/O interface when no external potential is applied. Since the Tafel-slopes of the different reactions are quite constant the Tafel slope is further denoted by \( b \). The rate of the reactions at the O/S interface is obtained by combining eqs. 4.16, 4.20 and 4.21.

\[ k_i = k_i^+ \exp(a b E) \] (4.23)
where

\[ k_i^+ = k_i^o \exp(y b p H) \] (4.24)

The expression for \( k_i \) at the M/O interface is more difficult to obtain. The reason is that the potential drop in the oxide film also depends on the applied potential \( E \), as is demonstrated in appendix 1. Similarly as for the O/S interface, the expression for \( k_i \) at the M/O interface is obtained by combining eqs. 4.15, 4.16, 4.20 and 4.22, yielding

\[ k_i = k_i^o \exp\left[ b\left(-\gamma p H - \phi_{o0} + \phi_{\text{ref.}}\right)\right] \exp\left[-b \phi_{f}\right] \exp\left[-b \phi_{m0}\right] x \exp[(1-\alpha) b E] \] (4.25)

The potential dependence of \( \phi_f \) in eq. 4.25 is obtained from the steady state thickness of the oxide film, which is derived in appendix 1:

\[ \exp(-b \phi_f) = \frac{k_5 C_h^\alpha}{k_2^*} \exp[-(1-\alpha) b E] \] (4.26)
where

\[ k_2^* = k_2^o \exp\left[ b\left(-\gamma p H - \phi_{o0} + \phi_{\text{ref.}}\right)\right] \exp\left[-b \phi_{m0}\right] \] (4.27)

The expression for \( k_i \) at the M/O interface is obtained by combining eqs. 4.25, 4.26 and 4.27, yielding
\[ k_i = k_i^0 \frac{k_S C_i^N}{k_2^0} \]  \hspace{1cm} (4.28)

It is clear that the reaction rates \( k_i \) at the M/O interface are constant. So the applied potential \( E \) causes a potential drop \( \alpha E \) at the O/S interface and \( (1-\alpha)E \) in the oxide film.

- For impedance measurements a small external voltage perturbation \( \Delta E \), is superimposed onto a dc potential \( E_{dc} \). As a consequence the reaction rate \( k_i \) is slightly varying with \( k_i + \delta k_i \). As was discussed before, the interfacial potential \( \phi_{m/o} \) is not a function of the applied potential \( E \). Hence the reaction rate is constant. The fluctuation of the reaction rates at the O/S interface \( \delta k_i \) is obtained by differentiating eq. 4.23 with respect to \( E \), using eq. 4.24:

\[ \delta k_i = \alpha b k_i \]  \hspace{1cm} (4.29)

where
\[ k_i = k_i^0 \exp\{\alpha b E\} \]  \hspace{1cm} (4.30)

### 4.4.4 Current-potential relation

Macdonald et al have calculated a general expression of \( i_{ss} \) as a function of the applied potential for an oxide \( MO_{x/2} \). In this section their derivation is given, but directly applied for the oxide film on aluminium (Al₂O₃). The calculation of \( i_{ss} \) is based on the fact that the dissolution rate of the passive film according to reaction 4.8, is equal to the passive film growth rate. In section 4.4.1 it was shown that the point defect model predicts passive film growth only due to reaction 4.5. Consequently only oxygen ion vacancies migration across the oxide film is responsible for the film growth:

\[ \frac{dL^+}{dt} = \frac{3}{2} \Omega_I J_o \]  \hspace{1cm} (4.31)

in which \( \Omega_I \) is the molar volume of aluminium oxide. The oxide dissolves chemically at the O/S interface, yielding
\[
\frac{dL^-}{dt} = k_{5n}C^n_H
\] (4.32)

in which \(n\) is the reaction order of reaction 4.8, and \(C_H\) the concentration of hydrogen ions. In steady state condition the rates of these two processes are equal, yielding:

\[
J_0 = \frac{2}{3}k_{5n}C^n_H
\] (4.33)

An expression for \(i_{ss}\) is obtained by combining the rule of charge conservation and Faraday's law. The direction of the electron and oxygen vacancies flux is opposite to the direction of the aluminium ion vacancies flux, yielding for the (passive) current \(i_{ss}\):

\[
i_{ss} = FJ_e = F(3J_{Al} + 2J_0)
\] (4.34)

in which \(F\) is Faraday's constant, \(J_e\) is the electron flux, \(J_0\) the oxygen anion vacancies flux and \(J_{Al}\) the aluminium cation vacancies flux across the film. Eq. 4.34 shows that in steady state condition, the current density depends on the fluxes of the anion and cation vacancies across the film. So these fluxes must be expressed in terms of the reaction rates of the interfacial reactions. The oxygen ion flux is given by eq. 4.33, in terms of the chemical dissolution rate. Note that this rate is equal to the rate of the film growth. The flux of aluminium ion vacancies across the oxide is more difficult to obtain. For steady state conditions the production of aluminium ion vacancies, eq. 4.6, is equal to the consumption rate of the vacancies, eq. 4.4. The equilibrium concentration of aluminium ion vacancies, \(C_{Al}\), is given by

\[
C_{Al} = \frac{k_3}{k_1}
\] (4.35)

When the rate of eq. 4.6 is quite smaller than that of eq. 4.4, depletion of vacancies occurs at the M/O interface. The current is then controlled by the supply of vacancies to the interface and hence a limiting current will be observed. Alternatively, reaction 4.6 can be much faster than reaction 4.4. For this case, no
limitation will occur and the flux of aluminium ion vacancies across the oxide can be expressed in terms of the rate of reaction 4.6:

\[ J_{Al} = k_3 \]  
(4.36)

The steady state current density follows from eqs. 4.33, 4.34 and 4.36:

\[ i_{ss} = F\left(3k_3 + \frac{4}{3}k_5C_H^0\right) \]  
(4.37)

Combination of eq. 4.37 with eqs. 4.16, 4.20, and 4.21, yields:

\[ i_{ss} = 3Fk_3^\gamma \exp(\gamma b pH) \exp(\alpha b E) + \frac{4}{3}Fk_5C_H^n \]  
(4.38)

Vetter\textsuperscript{2} stated that the overall current is sum of the current density for the formation of the oxide film (eq. 4.5) and the current density due to the dissolution of aluminium ions (eq. 4.6). Eq. 4.38 agrees with the current expression proposed by Vetter since the second term on the right hand side of eq. 4.38 is equal to the film growth rate.

Since the oxide film on aluminium is thermodynamically quite stable, the driving force for dissolution is rather small. The second term on the right hand side of eq. 4.38 is then rather small compared to the first term. This assumption means that \( J_{Al} \gg J_0 \). The logarithm of the current density should be proportional to both the applied potential \( E \) and the pH of the solution.

\[ i_{ss} \approx 3Fk_3^\gamma \exp(\gamma b pH) \exp(\alpha b E) \]  
(4.39)

### 4.4.5 Impedance of the passive film

In section 4.3.2 it was discussed that different processes occur at the interfaces of the oxide film and in the oxide film. Macdonald suggested that each of these processes can be represented as an impedance\textsuperscript{44}. The processes at the metal-oxide interface are represented as \( Z_{mo} \) and those at the oxide-solution interface as \( Z_{os} \). The film impedance is denoted as \( Z_f \). Without providing theoretical evidence Macdonald stated that the overall impedance, \( Z_{tot} \), may simply be
written as the sum of the impedances of both interfaces and the impedance of the oxide film itself.

\[ Z_{\text{tot}} = Z_{\text{mo}} + Z_f + Z_{\text{os}} \]  

(4.40)

Because the elements are connected in series, the largest impedance will dominate the total impedance. However, the impedance elements are frequency dependent, so that each of the elements may dominate over different frequency ranges.

Let us now consider the impedances of the metal-oxide and oxide-solution interface, and the impedance of the oxide film as was suggested by Macdonald et al.

At first approximation, the impedance of the metal-oxide interface can be represented by a simple parallel circuit consisting of charge transfer resistances and an interfacial double layer capacitance. The overall charge transfer resistances consist of the resistances of the electrons and aluminium cations transfer. Macdonald assumed that the charge transfer resistance of the electrons is quite small compared to that of the aluminium cation transfer. For frequencies in the range between 0.1 mHz and 10 kHz, it was shown that the total impedance is roughly equal to the resistance of the electron transfer over the M/O interface\textsuperscript{44}.

At the oxide-solution interface a more complicated reaction mechanism is generally occurring, resulting in a rather complex impedance. For simplicity, this interface is often represented by a parallel circuit of a charge transfer resistance and a double layer capacitance. Inductive loops, as result of adsorbed intermediates at the substrate-solution interface, may also be added to this impedance\textsuperscript{3-5}. An inductive element in a circuit means that the charge transfer is retard by the adsorbed intermediates, in particular when they are strongly adsorbed.

Chao, Lin and Macdonald\textsuperscript{40} derived an impedance expression for the oxide film based on the point defect model. They assumed that the reaction rates are quite fast. So, quasi-equilibrium at the interfaces exists, yielding equilibrium concentration of the aluminium and oxygen ion vacancies at the interfaces. Hence the overall process is controlled by diffusion of the vacancies from and to the interfaces. The impedance of the oxide film is then determined by the transport properties of vacancies across the oxide film. In the model it is assumed that the current is the sum of the rates of electrons, holes, aluminium ion and oxygen ion
vacancies across the oxide. Electron transport across the film was considered to be rapid and the electrons will "see" the oxide as a resistor. Likewise, the oxide is also proposed to be a resistor for the holes. The total impedance of the oxide film is therefore described in terms of the transport of vacancies in parallel with electron and hole resistances. Chao et al showed that the passive film behaves as a Warburg type of impedance for the transport of oxygen and aluminium ion vacancies across the film.

\[ R_{\text{mic}} = R_{\text{ct,e}} \]

\[ W_{V_0} \]

\[ W_{V_{AI}} \]

\[ R_H \]

\[ R_e \]

\[ C_{os} \]

\[ R_{os} \]

\[ R_S \]

**Figure 4.7** The electrical equivalent circuit according to Macdonallds approach for the calculation of the impedance of a passive film.

In summary, the overall impedance of a passive layer can be calculated using eq. 4.40. It can also be represented as the electrical equivalent circuit shown in figure 4.7. It should be noted that this circuit is only valid for quasi-equilibrium at the interfaces. The interfacial reactions are thus hardly anodically polarised. Figure 4.8 shows the corresponding impedance plot is of this circuit.

\[ R_S = 10 \Omega, \quad R_{os} = 1000 \Omega, \quad R_o = 1000 \Omega, \quad C_{os} = 10^{-6} F, \quad W = 1 e^{-8}. \]

**Figure 4.8** Impedance plot of the electrical equivalent circuit, shown in figure 4.5. Parameters: \( R_S = 10 \Omega, \) \( R_{os} = 1000 \Omega, \) \( R_o = 1000 \Omega, \) \( C_{os} = 10^{-6} F, \) \( W = 1 e^{-8}. \)
Recently Macdonald and Smedley\textsuperscript{38,39} calculated the transfer function of the oxide film for the case that the interfacial reactions were incorporated into the reaction mechanism. They assumed that the reactions were in a quasi-equilibrium state. The author of this thesis was not able to verify the derivation of the transfer function, which was very briefly described in reference 38 and 39. The calculation was based on the flux formula, eq. 4.34. Macdonald et al argued that for high frequencies the impedance of the O/S interface dominated the overall impedance, yielding a capacitive semi-circle in a Nyquist plot. At low frequencies their transfer function showed a Warburg impedance due to either anion or cation ion vacancies transport across the oxide. The Nyquist plot of the transfer function is similar to the Nyquist plot shown in figure 4.8. Macdonald found that the calculated transfer function did describe the impedance data of Nickel in a phosphate buffer solution (pH=11) quite well.

In section 4.4.4 it was discussed that the point defect model predicts a constant potential drop at the M/O interface. As a consequence fluctuations of the applied potential do not effect this interfacial potential. Hence this interface is represented by a charge transfer resistance. Although the interfacial double layer capacitance is present, it is not charged and decharged and can be safely neglected. The representation of the M/O interface by a resistance in figure 4.7 is thus correct. The measured impedance can therefore be attributed to the oxide film and to processes occurring at the O/S interface.

4.4.6 Application of PDM to our measurements

Macdonald's point defect model is able to describe the impedance measurements of passive aluminium in the potassium sulphate and sodium nitrate solutions quite well (compare fig. 4.3 and fig. 4.8). According to the point defect model, the observed Warburg impedance can be attributed to the transport of either oxygen ion vacancies or aluminium ion vacancies across the oxide film. The time constant at high frequencies (semi-circle in fig. 4.3) is due to the charge transfer reactions at the O/S interface.

The point defect model can not describe the impedance measurements, which have an inductive loop at intermediate frequencies (see fig. 4.2). From literature it became clear that adsorbed charged intermediates may result in an inductive loop\textsuperscript{3-5}. Adsorbed intermediates hinder the charge transfer, in a similar way as
the inductive current due to a fluctuating magnetic field across an inductor, counteracts the cause of its existence. This is more pronounced when the intermediates are strongly adsorbed. In sections 4.4.4 and 4.4.5 it was discussed that only the processes at the O/S interface and the oxide film itself contribute to the measured impedance since the M/O interfacial potential is constant. Therefore the presence of an inductive loop in the impedance plot indicates that adsorbed species are present at the interface. A possible candidate, suggested by Valand and Heusler\(^\text{15}\), is an adsorbed oxygen ion. As mentioned in section 4.3.2, Valand and Heusler\(^\text{15}\) suggested that adsorbed oxygen ions are formed by the dissociation of water at the O/S interface. The incorporation of adsorbed oxygen ions in the oxide lattice is the rate determining reaction (see eqs. 4.1 to 4.3). Furthermore, in section 4.4.1 it has been shown that the overall reaction 4.7 can be split into two reactions, eqs. 4.10 and 4.11. The incorporation of an adsorbed oxygen ion in the oxide lattice is only possible when an oxygen ion vacancy is present at the O/S interface, according to eq. 4.11. The rate determining step of the mechanism of Valand and Heusler, eq 4.3, is equivalent to reaction 4.11.

Reaction 4.11 is slow when for example the concentration of oxygen ion vacancies at the O/S interface is relatively small due to a low production rate at the M/O interface (reaction 4.5 is slow, hence \(k_2\) is small) and a slow transport process of the vacancies across the layer. Hence a relatively large concentration of (adsorbed) oxygen anions exists, which results in an inductance. Cations and anions from the electrolyte solution may specifically adsorb at the O/S interface and hence block the oxygen ion vacancies for the (adsorbed) oxygen ions. This is plausible since the impedance plots are quite different for certain electrolyte solutions. Specific adsorption of anions and cations can be studied by recording electrocapillary curves. In this curve the surface tension is measured as a function of the potential. At the potential of zero charge the curve has a maximum. This maximum shifts to more negative potentials when anions are specifically adsorbed. This is due to the fact that these adsorbed ions repel each other, resulting in a smaller surface tension. The results of these electrocapillary measurements on mercury showed that sodium and potassium cations are not specifically adsorbed in contrast to the larger cations as rubidium and cesium. Sulphate anions are only slightly adsorbed whereas ions like chloride are specifically adsorbed. It should be noted that nitrate anions are strongly adsorbed specifically. Although these results concern mercury, specific adsorption at the surface of the passive layer on aluminium will certainly also occur.
Figure 4.9  Polarisation curves of pure aluminium in a 0.1 M NaOH solution (a), and in a 1 M sulphuric acid solution (b). Polarisation curve of an Al 5050 alloy in a 0.1 M sodium sulphate solution with pH = 5.8 (c).

Figure 4.9 shows the polarisation curves of passive aluminium in sodium hydroxide, sulphuric acid and sodium sulphate solution. The impedance plots for
these measurements showed an inductive loop at intermediate frequencies. A linear relation between the current density and the potential is observed in figure 4.9. This was also reported by Brett for measurements in chloride solutions\textsuperscript{29}. In section 4.4.4 the current-potential relation was derived. There it was assumed that the oxygen ion vacancy flux across the oxide, which was equal to the chemical dissolution rate of the oxide layer, is small compared to the aluminium ion vacancy flux. It is noted that, according to MacDonalds point defect model, aluminium ion vacancies only pass the oxide layer. They do not result in film growth. For such a cation conductive oxide, eq. 4.39 describes the current-potential relation. The linear relation found in figure 4.9 can only be explained when the factor $\alpha bE$ in the exponential term in eq. 4.39 is assumed to be quite small. So, the factor $\alpha b$ should be quite small. The parameter $b$ is the inverse of the Tafel slope, which is usually in the order of 100mV. This implies that the parameter $\alpha$ should be quite small. Expanding the exponential term of eq. 4.39 in $\alpha bE$, yields

$$i_{ss} = 3Fk_3^5 \exp(\gamma b pH) \{1+\alpha bE\} \quad (4.41)$$

In figure 4.10 the polarisation curve of aluminium in a 0.1 M sodium nitrate solution is shown. Similar polarisation curves and impedance plots are obtained in potassium sulphate and nitric acid solutions. Both the Warburg impedance response, observed in the impedance plot at low frequencies, and the limiting current at anodic potentials indicate that the overall corrosion behaviour is controlled by a diffusion process. The origin of the diffusion process is not clear. Ions from the electrolyte solution play certainly a major role as was already concluded in section 4.3.3. The diffusion limitation can be caused by reaction 4.4, i.e. the consumption reaction of aluminium ion vacancies at the M/O interface. This was already discussed in section 4.4.4 at the derivation of eq. 4.36. Diffusion limitation may occur when the rate of reaction 4.6 (i.e. the production rate of aluminium ion vacancies) is smaller than that of reaction 4.4, or when the transport properties of the oxide layer control the aluminium ion vacancies flux across the layer. The consumption rate of aluminium vacancies at the M/O interface (eq. 4.4) does not vary with the externally applied potential since the potential drop at the M/O interface is constant. However the production rate of aluminium ion vacancies at the O/S interface (eq. 4.6) increases with more positive externally applied potentials. Despite this, diffusion limitation may occur when anions from the electrolyte solution adsorbed specifically at the O/S
interface and hence considerably diminish the production rate of aluminium ion vacancies. Adsorbed ions may exclude some surface area for reaction 4.6 to occur, resulting in a decrease of the production rate. The competition between the increase of reaction rate 4.6 at more anodic potentials on one hand, and the decrease of the reaction rate due to specific adsorption on the other hand, may be deduced from the impedance results of aluminium in potassium sulphate solutions. In these solutions a diffusion limitation at anodic potentials is observed, showing a Warburg impedance response. Specific adsorption will decreases the production rate of aluminium ion vacancies at the O/S interface considerably, as discussed before. At very positive potentials however the current density does again slightly increase. The Warburg impedance changes then into a (very large) semi circle and a (small) inductance is also observed. When the applied potential increases, more adsorbed oxygen ions are produced by the water dissociation reaction rate 4.10. For the measurements in potassium sulphate solutions, the adsorbed anions from the electrolyte solutions are displaced by adsorbed oxygen ions at very positive anodic potentials, resulting in an inductive loop. For the nitrate solutions however the strongly adsorbed anions are not displaced. No inductive loop is observed.

![Graph showing polarization curve of aluminium in a 0.1 M sodium nitrate solution](image)

Fig. 4.10 Polarisation curve of aluminium in a 0.1 M sodium nitrate solution

Polarisation curves have been recorded for aluminium in sulphuric acid and sodium sulphate solutions of different pH (fig. 4.11). From these curves, the relation between the pH and the current density was determined and plotted in figure 4.12. According to eq. 4.39, the sign of parameter $\gamma$ can be determined from the slope in figure 4.12. Parameter $\gamma$ is negative. When the pH is decreasing the
concentration of hydrogen ions increases, resulting in a more positive potential drop.

Figure 4.11 Polarisation curves for pure aluminium in a 1 M sodium sulphate solution at different pH's.

Figure 4.12 The current density at -500 mV as a function of the pH for pure aluminium in 1 M sodium sulphate solution.

Accurate analysis of the impedance plots using the Equivcrt software\textsuperscript{12} showed that four time constants could be determined for the impedance measurements which have an inductance. Macdonalds point defect model shows however two time constants: one time constant for the O/S interface and one for the oxide layer (see fig. 4.7). It is noted that the Warburg elements in figure 4.7 can be represented by one Warburg element. This holds also for the resistances. Therefore one time constant represents the oxide film. Since figure 4.2 shows no diffusion response, the Warburg elements in figure 4.7 can be neglected and
hence only a resistance represents the oxide layer impedance. In section 4.3.1 it was mentioned that the oxide layer on aluminium may behave as a dielectric material. Therefore a capacitance should be added parallel to the resistance of the oxide layer. This results in one time constant, representing the oxide layer. In summary one can say that Macdonalds point defect model and its small modifications (dielectric behaviour of the oxide film) show only two time constants whereas four time constants were determined in the measured data. Thus, the point defect model has to be modified.

The preliminary analysis of the impedance data shows that the mechanism of passive film growth is influenced by several factors as for example the potential, the pH of the solution and the nature of the electrolyte solution. It became clear that the inductive loop is the result of the presence of adsorbed oxygen ions at the O/S interface. So, the dissociation reaction of water at the O/S interface should be incorporated into the reaction mechanism. Another modification of Macdonalds point defect model, resulting in an additional time constant, is the adsorption of anions from the electrolyte solution, which may result in a diffusion control of reaction 4.4. This is discussed in the next section where the transfer function is calculated.

4.5 Point Defect Model, A Revised Model

4.5.1 Reaction mechanism

In this section, the Macdonald’s point defect model is adjusted. Two major changes are proposed. The first one is that water is dissociated at the oxide surface, providing an adsorbed oxygen ion. This was also suggested by Valand et al. This reaction is not potential controlled. In section 4.4.1 it was already demonstrated that the overall reaction 4.7 can be split in a dissociation and an incorporation reaction.

\[ \text{Dissociation:} \]
\[ H_2O \xrightleftharpoons[k_7 \cdot k_8]{k_{-7}} O_{ad}^{2-} + 2H^+ \quad (4.10) \]

\[ \text{Incorporation:} \]

The adsorbed ion can be oxidised according to two pathways.
where $k_7$ is the forward reaction rate and $k_7$ the backward reaction rate. Eqs. 4.10 and 4.11 yields reaction 4.7 which is in fact the bruto reaction. Similarly, eqs. 4.10 and 4.42 yields eq. 4.13. This way reaction 4.13 is incorporated into the model. Hence the oxide films will also grow on the oxide-solution interface. In this thesis it is assumed that this reaction is quite slow and it will thus be neglected.

![Figure 4.13](image)

*Figure 4.13 The corrosion processes occurring at an aluminium - electrolyte solution interface. The different reactions are discussed in the text.*

Figure 4.13 shows schematically the different reactions occurring at the O/S interface. The dissociated water yields a layer of adsorbed oxygen ions on the aluminium oxide surface. An adsorbed oxygen ion can be incorporated into the oxide when it meets an oxygen ion vacancy at the surface ($k_8$). Also anions from the electrolyte solution adsorb on the interface. At a kink site aluminium ions in the lattice may dissolve, leaving an aluminium ion vacancy. It should be noted that the oxide may also chemically dissolve. This occurs preferably at a kink-site or other lattice defects where the coordination number of the atoms is small.
4.5.2 Principle of the transfer function calculation

In this section the principle of the transfer function calculation is discussed for the case that there is no quasi-equilibrium at the interfaces. The interfacial reactions are anodically polarised to such extend that the backward reaction rate can safely be neglected. The overall impedance can be calculated using eq. 4.15 for the potential-distance relation across the metal-oxide-solution system.

\[ E + \phi_{\text{ref.}} = \phi_{\text{mo}} + \phi_{\text{f}} + \phi_{\text{os}} \]  

(4.15)

Superimposing a potential perturbation of \( E \), \( \delta E \), onto the dc potential \( E \) results in fluctuations of the potential drop at the O/S interfaces and that in the oxide film. The other potentials are constant, i.e. the potential drop at the M/O interface and that of the reference electrode solution interface. So one finds

\[ (E + \delta E) + \phi_{\text{ref.}} = \phi_{\text{mo}} + (\phi_{\text{f}} + \delta \phi_{\text{f}}) + (\phi_{\text{os}} + \delta \phi_{\text{os}}) \]  

(4.43)

and combining with eq. 4.15, yields

\[ \delta E = \delta \phi_{\text{f}} + \delta \phi_{\text{os}} \]  

(4.44)

Since the current, and so its fluctuation, should be constant across the system,

\[ \delta i = \delta i_{\text{f}} = \delta i_{\text{os}} \]  

(4.45)

the impedance, defined as \( Z = \frac{\delta E}{\delta i} \), becomes

\[ Z = Z_{\text{f}} + Z_{\text{os}} \]  

(4.46)

where \( Z_{\text{f}} = \frac{\delta \phi_{\text{f}}}{\delta i} \) and \( Z_{\text{os}} = \frac{\delta \phi_{\text{os}}}{\delta i} \).

This expression is closely equal to the overall impedance expression of Macdonald, eq. 4.40. Note that in Macdonald's model the impedance of the M/O interface was given by a resistance. As discussed in section 4.4.4 this is due to the constant potential at this interface.
4.5.3 The calculation of the transfer function

In this section the interfacial impedances will be calculated, using the revised point defect model. The total impedance (transfer function) is obtained by applying eq. 4.46. The most important steps for the calculation of the interfacial impedances are now successively given. The essential equations are related to the conservation of mass and charge. First the impedance of the oxide film is calculated and then the impedance of the O/S interface. First order reaction kinetic is assumed since reactions 4.11 and 4.42 are elementary reactions.

*Impedance of the passive film*

The potential drop in the passive film, $\phi_f$, has been calculated as a function of the potential in section 4.5.2. It was shown that the potential drop increases in approximation linearly with the externally applied potential. From this expression the admittance of the oxide film can be calculated (see eqs. 4.18 and 4.19). It is assumed that the passive film behaves as a resistor for electrons and holes. Their values are denoted by $R_e$ and $R_h'$. Since the oxide is a semi-conductor, the capacitance of the oxide film should be added to the admittance. So, one finds for the total admittance of the oxide film $Y_f$:

$$Y_f = \frac{1}{R_f} + j\omega C_f$$  \hspace{1cm} (4.47)

where $R_f = R_e + R_h'$.

*Impedance of the O/S interface*

The impedance is calculated using the mass and charge balances. *the mass balances are*

$$J_{Al} = k_3 (1 - \theta_{ao} - \theta_{aa})$$  \hspace{1cm} (4.48)

$$J_o = \frac{2}{3} k_8 C_o \theta_{ao} \beta$$  \hspace{1cm} (4.49)

where $\theta_{ao}$ is the fraction of the surface covered by adsorbed oxygen ions, $\theta_{aa}$ is the fraction of the surface covered by adsorbed anions from the electrolyte solution. The following differential equation holds for the surface fraction, covered by the adsorbed oxygen ions:
\[ \beta \frac{d\theta_{ao}}{dt} = k_7 (1 - \theta_{ao} - \theta_{aa}) - k_{-7} \theta_{ao} \beta C_H^2 - k_8 C_0 \theta_{ao} \beta \]  

(4.50)

where \( \beta \) is the maximum number of sites per unit surface area which can be occupied by the adsorbed oxygen ion. An expression for the concentration adsorbed anion at the interface is more difficult to obtain. Mohilner\textsuperscript{45} gives an review on the double layer capacitance and the role of specific adsorption. Most work on adsorption concerns equilibrium situations (thermodynamics) of neutral substances. Knowledge of the rate of adsorption processes is however also important for many studies of the kinetics of charge transfer processes. The adsorption of a substance \( h \) can formally be represented as a exchange reaction between adsorbed ions, available sites and the activity of anions in the solution:

\[ h + S \xrightleftharpoons[k_{-11}]^{k_{11}} A \]  

(4.51)

where \( S \) represents a site on the electrode surface and \( A \) the adsorbed species. \( k_{11} \) is the forward reaction rate and \( k_{-11} \) the backward reaction rate. Mohilner stated that the exchange of species (e.g. ions) between the adsorbed state and the "free" state, i.e ions in the solution, can be described similarly as the charge transfer process. The reaction rate of adsorption is thus a function of the externally applied potential. As a first approach we assume that the potential dependence of the surface fraction occupied by anions from the electrolyte solution is rather small. Hence it is assumed to be constant. The equilibrium surface concentration anions depends however on the anion type.

In steady state the left hand side of eq. 4.50 is equal to zero. Then the surface concentration of adsorbed oxygen ion at the surface is obtained from eq. 4.50, yielding:

\[ \theta_{ao} = \frac{k_7}{k_7 + k_{-7} \beta C_H^2 + k_8 C_0 \beta} (1 - \theta_{aa}) \]  

(4.52)

The surface concentration of adsorbed oxygen ion will be quite small when \( k_8 \) is relatively large compared to \( k_7 \), or when the backward reaction, \( k_{-7} \), is quite fast. On the other hand the surface concentration will be equal to unity when the reaction rates \( k_{-7} \) and \( k_8 \) are relatively slow, compared to \( k_7 \). Eq. 4.52 shows that
there is a competition between the concentration anions from the electrolyte and the concentration adsorbed oxygen anions.

Charge conservation at the O/S interface yields

\[ i = \nabla F \left\{ 3k_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}k_8C_0\theta_{ao}\beta \right\} \]

(4.53)

When a small perturbation of the potential $E$ is applied to the steady state, the current response $\delta i$ is

\[
\delta i = F \left\{ 3k_3b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}k_8b_8C_0\theta_{ao}\beta \right\} \alpha \delta E + F \left\{ \frac{4}{3}k_8C_0\beta - 3k_3 \right\} \delta \theta_{ao} + F \left\{ \frac{4}{3}k_8\beta \theta_{ao} \right\} \delta C_0
\]

(4.54)

where $\delta \theta_{ao}$ is the response of the potential perturbation:

\[ \delta \theta_{ao} = \theta_m \exp[j(\omega t + \phi_1)] \]

(4.55)

where $\phi_1$ is a phase shift. No diffusion limitation is observed and therefore the last term on the right hand side of eq. 4.54 is neglected. Applying eq. 4.55 to the mass balances, eq. 4.50, an expression for $\delta \theta_{ad}$ is obtained:

\[ \delta \theta_{ao} = \frac{-k_8b_8C_0\theta_{ao}\beta}{\left\{ j\omega \beta + k_7 + k_{-7}C_H^2 + k_8C_0\beta \right\}} \alpha \delta E \]

(4.56)

The total admittance $Y = \frac{\delta i}{\delta E}$ is obtained from eqs. 4.54 and 4.56, yielding:

\[
Y_{os} = F \left\{ 3k_3b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}k_8b_8C_0\theta_{ao}\beta \right\} \alpha + F \left\{ 3k_3 - \frac{4}{3}k_8C_0\beta \right\} \frac{k_8b_8C_0\theta_{ao}\beta}{\left\{ j\omega \beta + k_7 + k_{-7}C_H^2 + k_8C_0\beta \right\}} \alpha + j\omega C_{os}
\]

(4.57)
Eq. 4.57 is a quite complicated admittance expression. The admittance $Y$ of eq. 4.57 can be represented as

$$Y_{os} = \frac{1}{R_{ct}} + \frac{A}{B + D j\omega} + j\omega C_{os} \quad (4.58)$$

where

$$\frac{1}{R_{os}} = \left[3k_3b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}k_8b_8c_0\theta_{ao}\beta\right]\alpha \quad (4.59)$$

$$A = \left(3k_3 - \frac{4}{3}k_8c_0\beta\right)k_8b_8c_0\theta_{ao}\beta\alpha \quad (4.60)$$

$$B = k_7 + k_7\beta c_{hi}^2 + k_8c_0\beta \quad (4.61)$$

$$D = \beta \quad (4.62)$$

The admittance of the O/S interface can be represented in the equivalent circuit shown in figure 4.14. It should be noted that the second term of the right hand side of eq. 4.58 can be considered as a series connection of a resistor and an inductor since parameter $A$ in eq. 4.58 is always positive, i.e. $\left(3k_3 - \frac{4}{3}k_8c_0\beta\right) > 0$ (see eq. 4.60).

![Figure 4.14 An equivalent circuit, representing the O/S interface](image)

The transfer function, represented by the equivalent circuit of figure 4.14, contains an inductive component. This means that the inductive loop, observed in our impedance measurements (fig. 4.2) can indeed be attributed to adsorbed oxygen ions at the O/S interface.
**Calculation of the overall impedance**

The total impedance of the entire passive layer has to be calculated by applying eq. 4.46. The expressions for \( Y_f \) and \( Y_{os} \) were given before, see eqs 4.47 and 4.58. The total impedance can be represented in terms of the equivalent circuit of figure 4.15.

![Equivalent circuit diagram](image)

*Figure 4.15 An electrical equivalent circuit representing the revised point defect model of an oxide layer*

The revised model of the point defect model shows three time constants. The oxide film contributes to the overall impedance with a single time constant. Two time constants originate from the O/S interface, i.e. one due to the charge transfer reactions and one due to the oxygen ions absorbed at the surface.

**4.6 Application of the revised model to our measurements**

The impedance data were analysed using Equivcrt to obtain the number of time constants. As mentioned before, four time constants could be determined. The
revised model predicts however three time constants (see fig. 4.15). The two time constants at high frequencies are probably due to the oxide film and the charge transfer reactions at the O/S interface. The inductance at intermediate frequencies can be attributed to the adsorbed oxygen ions at the O/S interface as was derived in the previous section. Finally the origin of the time constant at low frequencies is not clear. Several processes may cause an additional time constant. First, the incorporation of eq. 4.42 into the model would lead to an
additional time constant since the potential drop at the M/O interface becomes then a function of the externally applied potential. This admittance is difficult to obtain analytically due to the fact that the equations at the interfaces become coupled. It is expected that the potential drop at the M/O interface is rather small. Hence the diameter of the semi-circle is quite large, which is indeed observed for the time constant at low frequencies. Secondly, the adsorbed anions from the electrolyte solution may yield an additional time constant. As discussed in the previous section, the adsorption process can be considered similarly as a charge transfer reaction. Now the differential equation for the adsorbed oxygen ions, eq. 4.50, becomes coupled with the differential equation, describing the change of the surface fraction occupied with adsorbed anions with time.

To obtain an accurate fit, an extra time constant was added in series with the model in fig. 4.15. In figure 4.16 a typical Nyquist and Bode plot of an impedance measurement and its fit are shown. This figure also shows the error plot given by the fitting program. The quality of the fit met the rules for acceptable fits, discussed in section 4.2.2. The capacitive circle at high frequencies consists of two strongly overlapping time constants. This can be observed from the phase angle of the Bode plot in figure 4.16. The phase angle is constant in the frequency range between 15 and 5000 Hz, indicating two overlapping time constants.

The model with the extra time constant was fitted to the impedance measurements performed at several anodic potentials and to the measurements performed in solutions of different pH. The purpose of this was to determine the relation of the circuit elements with the applied potential and the pH of the solution. These relations were compared with the expected relation according to the revised point defect model. The fit results of the impedance data are analysed in more detail in section 4.6.1 (potential dependence) and in section 4.6.2 (pH dependence).

4.6.1 Potential dependence
The following assumptions have to be made in order to calculate the potential dependence of the expressions for the components of the equivalent circuit. In appendix 2 the derivation of the potential and pH dependence is given. Here only the highlights are discussed.
For a cation conducting oxide the concentration of adsorbed oxygen ions at the O/S interface is relatively large. As discussed in section 4.4.6 this may be attributed to the relatively low concentration of oxygen ion vacancies at this interface since the production rate is quite small (eq. 4.5, reaction rate \( k_2 \)). Note that the film growth reactions 4.5 is equal to the rate of the chemical dissolution reaction, which was assumed to be quite small. In addition specific adsorption of anions from the electrolyte solution may block a fraction of the O/S surface. Hence reaction 4.11 (\( k_8 \)) is quite slow.

The equilibrium concentration of adsorbed oxygen ions is given by eq. 4.52. We discussed before that \( k_6 \) is small. When the backward reaction of the water dissociation at the O/S surface, eq. 4.10, is assumed to be slow, the adsorbed oxygen ions cover a relatively large surface area. The fraction of the surface, covered with adsorbed oxygen ions, is then approximately equal to

\[
\theta_{ao}^{ss} = \left(1 - \frac{k_7 \beta C_H^2}{k_7} - \frac{k_8 \beta C_0^2}{k_7}\right) (1 - \theta_{aa})
\]  

(4.63)

The equilibrium concentration of oxygen ion vacancies at the O/S interface can be determined from the production rate at the M/O interface, \( k_2 \), (eq. 4.5) and the consumption rate at the O/S interface (eq. 4.49), yielding

\[
C_0 = \frac{k_2}{k_8 \theta_{ao} \beta}
\]

(4.64)

The fraction of the surface, covered with adsorbed oxygen ions, is obtained by combining eqs. 4.63 and 4.64. This yields the following quadratic equation which should be solved.

\[
\left(\theta_{ao}^{ss}\right)^2 - \left(1 - \frac{k_7 \beta C_H^2}{k_7}\right) (1 - \theta_{aa}) \theta_{ao}^{ss} + k_2 (1 - \theta_{aa}) = 0
\]

(4.65)

The solution, i.e. the concentration oxygen vacancies at the O/S, is a function of the surface fraction of adsorbed anions, the reaction rate \( k_2 \), and the reaction rates of the water dissociation reaction, \( k_7 \) and \( k_7 \), which are all constants.
In section 4.4.6 it was concluded from the linear relation between the applied potential and the measured current, that the parameter $\alpha$ must be quite small. Eq 4.65 was used in the calculations. Applying all these assumptions the potential dependence of the components of the equivalent circuit is:

$$\frac{1}{R_{os}} = 3\alpha^2 k_3 b_2 (1 - \theta_{ao} - \theta_{aa}) E + 3\alpha k_3 b_3 (1 - \theta_{ao} - \theta_{aa}) + \frac{4}{3} \alpha k_2 b_8$$ (4.66)

$$\frac{1}{R_{ad}} = \frac{3k_3 k_2 b_3 b_8 \alpha^2 E + 3k_3 k_2 b_8 \alpha - \frac{4}{3} k_2 b_8 \alpha}{k_7 + k_2 \theta_{oa}}$$ (4.67)

$$\frac{1}{L_{ad}} = \frac{3k_3 k_2 b_3 b_8 \alpha^2 E + 3k_3 k_2 b_8 \alpha - \frac{4}{3} k_2 b_8 \alpha}{\beta}$$ (4.68)

In appendix 2 the complete derivation is given. Eqs 4.66 to 4.68 show that the components of the circuit should be inversely related to the applied potential $E$. The slope should be positive for all components. The ratio of the $R_{ad}$ and $R_{os}$ should vary linearly with the applied potential.

![Nyquist plot](image)

**Figure 4.17** Nyquist plot of aluminium in a 1 M sulphuric acid solution at several potentials. (○) -1100mV; (△) -1000mV; (+) -600mV; (OCP is -1321mV)
Figure 4.17 shows Nyquist plots of aluminium at several anodic potentials. The fit results for these potentials are also shown. The potential dependence of the different components of the equivalent circuit shown in figure 4.18, agrees quite well with the expected linear relation, given by eqs. 4.66 to 4.68. The value of the interfacial potential $C_{OS}$ is influenced by the fact that oxygen ions are adsorbed on the surface. Their presence may considerably effect the potential drop at the interface and in the double layer. In fact the linear increase of the inverse double layer capacitance suggests that the surface area covered by the adsorbed ions decreases linearly with the potential. This is not predicted by the revised model since the fraction of the surface occupied by the adsorbed oxygen ions is constant (eq. 4.65).

The oxide film capacitance decreases with the potential and shows also a linear relation between the inverse of the capacitance and the potential, similarly to the behaviour of $C_{OS}$. Applying the equation for a plane capacitor, and assuming that $\varepsilon_{Al_2O_3}$ is about 10, the thickness can be calculated as a function of the potential $E$. The thickness of the oxide film varies between 1.5 and 2.4 nm. The value of the resistance of the oxide film is about 1.1k$\Omega$. The specific resistance of the oxide has been calculated using Ohm law and is found to be about $1.5 \times 10^{11}$ $\Omega$cm. Kittel\cite{46} divided the electric behaviour in different categories: metal, semi-conductor and isolator. Each category has a characteristic value for the specific resistance. Semi-conductive behaviour is found when the specific resistance lies between $10^5$ and $10^9$ $\Omega$cm. The specific resistance of an isolator is larger than $10^{13}$ $\Omega$cm. Thus the passive film on aluminium can be considered as a very poor semi-conductor. From figure 4.18 it is concluded that the revised point defect model can account for the film growth of aluminium.
4.6.2 pH dependence

The pH dependence of eqs 4.66 to 4.68 can not be directly derived. The parameters \( k_1^* \) contain the pH, see eqs. 4.22 and 4.24. The pH dependence of the components is:

\[
\frac{1}{R_{os}} \propto \xi_1 \exp(\gamma pH) \tag{4.69}
\]

\[
\frac{1}{R_{ad}} \propto \xi_2 \exp(\gamma pH) \tag{4.70}
\]

\[
\frac{1}{L_{ad}} \propto \xi_3 \exp(\gamma pH) \tag{4.71}
\]

where \( \xi_1, \xi_2 \) and \( \xi_3 \) are positive constants. In section 4.4.6 it was shown that the parameter, \( \gamma \), is negative. Eqs. 4.69 to 4.71 show that a logarithmic relation is expected between the components of the equivalent circuit and the pH of the solution. The slope should be positive. Figure 4.19 shows the Nyquist plots obtained in solutions with different pH. The pH dependence of the different components of the equivalent circuit are shown in figure 4.20. From this figure it is
concluded that the revised point defect model can also account for the pH dependence. The deviations for pH values above 4.5 are attributed to the fact that then the oxide becomes thermodynamically stable and will not dissolve in the electrolyte solution. In our calculation this was a major assumption. Therefore these data points were not taken into account when the revised model was evaluated.

Figure 4.19 Nyquist plots of aluminium in 1M sodium sulphate solution of pH = 2.2 (○), pH = 3 (○), and pH = 5.7 (+).

a) $R_{\text{ox}}$ (Ω) vs. pH

b) $C_{\text{ox}}$ (x10^3 Ω cm^2) vs. pH
4.6.3 Influence of anion type

In this section the influence of anions form the electrolyte solution on the inductive loop is discussed. As mentioned before an inductive loop is only observed in the impedance plots when the adsorbed oxygen ions are present at the O/S interface.

When the fraction of adsorbed anions from the electrolyte solution increases (i.e. $\theta_{aa}$) the charge transfer resistance $R_{os}$, which is given by eq. 4.66, also increases. So the diameter of the first circle may increase. Nitrate anions are very strongly adsorbed, yielding a very large semi-circle for the time constant at high frequencies (see fig. 4.3). As the inductive loop for this case is very small, it will not be observed in the Nyquist plots.

Since the adsorption depends on the concentration of the ions of the electrolyte solution, it is expected that a larger fraction is occupied by them when the bulk concentration is larger. This is indeed observed in table 4.2. The diameter of the first semi-circle increases with increasing bulk concentration, indicating that adsorption of anions play a role.
Figure 4.21 The effect of anions on the inductive loop

a) (+) : 0.1 M sodium sulphate solution; (o) : 1 M sodium sulphate solution
b) (+) : 0.1 M HCl solution\textsuperscript{25}; (o) : 0.1 M sulphuric acid solution
c) (+) : 0.1 M HAc; (o) : 1 M sodium sulphate solution
Since the circle diameter of the first time constant are rather different for the measurements performed in different electrolyte solutions, the Nyquist plots are scaled to this diameter. Figure 4.21 shows the scaled Nyquist plots. Table 4.1 shows the maximum values for the real and imaginary part of the impedance which were used for scaling. From table 4.1 it is concluded that sulphate adsorbs more strongly than chloride.

<table>
<thead>
<tr>
<th>solution</th>
<th>pH</th>
<th>potential (mV)</th>
<th>Re$Z_{\text{max}}$ (kΩcm$^2$)</th>
<th>-Im$Z_{\text{max}}$ (kΩcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M Na$_2$SO$_4$</td>
<td>5.7</td>
<td>-630</td>
<td>8.682</td>
<td>4.333</td>
</tr>
<tr>
<td>1 M Na$_2$SO$_4$</td>
<td>5.7</td>
<td>-610</td>
<td>13.18</td>
<td>6.679</td>
</tr>
<tr>
<td>0.1 M HCl $^{25}$</td>
<td>1.1</td>
<td>-800 (SCE)</td>
<td>0.552</td>
<td>0.261</td>
</tr>
<tr>
<td>0.1M H$_2$SO$_4$</td>
<td>1.2</td>
<td>-970</td>
<td>1.265</td>
<td>0.575</td>
</tr>
<tr>
<td>0.1 M HAc</td>
<td>2.9</td>
<td>-560</td>
<td>154.4</td>
<td>73.16</td>
</tr>
<tr>
<td>1 M Na$_2$SO$_4$</td>
<td>=3</td>
<td>-610</td>
<td>6.47</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Table 4.2 Influence of anion type on the time constant at high frequencies

In figure 4.21 it is clearly visible that the inductive loops for the different electrolyte solutions strongly overlap. This indicates that the concentration of adsorbed oxygen ions is rather constant. This agrees with eqs. 4.67 and 4.68, which are mainly determined by reaction 4.6 ($k_3$). The adsorption of anions does hardly effect the values for $L_{\text{ad}}$ and $R_{\text{ad}}$ (eqs. 4.67 and 4.68)

4.7 Conclusions
The point model proposed by Macdonald can not describe the measurements of passive aluminium in most electrolyte solutions since the impedance plots show an inductive loop at intermediate frequencies. Four time constants have been determined. The passive film represents a time constant. At the O/S interface the charge transfer reactions and adsorbed oxygen ions yield two other time constants. Macdonalds original model predicts however only two time constants. The revised model may account for three time constants. Adsorbed oxygen ions can be incorporated into the reaction mechanism by the dissociation reaction of water. An inductive element in the equivalent is now obtained. Anions from the electrolyte solution may also interact with the oxide-solution interface. Their role
could only quantitative be understood. The fourth time constant may be related with these adsorbed anions. An alternative explanation would be the incorporation of reaction 4.42 into the reaction mechanism. The potential drop at the M/O interface is then a function of the externally applied potential, resulting in an additional time constant.

Appendix 1  The thickness of the passive film

In this appendix the relation between the thickness of the passive film and the applied potential \( E \) is derived. It should be noted that the derivation is given for the general case where the film growth occurs at both interfaces. The special case that the film growth at the O/S interface is neglected, is also discussed. This is equivalent to Macdonald's point defect model.

The thickness of the passive film can be calculated using the fact there is an equilibrium stage when the dissolution reaction of the oxide film, eq. 4.8, is equal to the film growth rate due to reactions 4.5 and 4.42. The film growth is

\[
\frac{dL^+}{dt} = \Omega_l (k_2 + k_{10}) \tag{A1.1}
\]

Applying eq. 4.16, 4.17, 4.20, 4.21 and 4.22, and the fact that \( b = b_{mo} = b_{os} \), one finds for the film growth rate

\[
\frac{dL^+}{dt} = \Omega_l k_2 \exp \left[ b \left( -\gamma_pH - \phi_{os}^* + \phi_{ref.} \right) \right] \exp (-b\varepsilon L) \times \\
\exp (-b\phi_{mo}^*) \exp [b(1-\alpha)E] + \Omega_l k_{10} \exp (b\gamma_pH) \exp (\alpha b E) \tag{A1.2}
\]

We rewrite eq. A1.2 as

\[
\frac{dL^+}{dt} = \Omega_l \left\{ k_2 \exp (-b\varepsilon L) \exp [b(1-\alpha)E] + k_{10} \exp (\alpha b E) \right\} \tag{A1.3}
\]

with

\[
k_{10}^* = k_{10} \exp [b\gamma_pH] \tag{A1.4}
\]
\[ k_2^* = k_2^* \exp[-b\phi_{mo}^*] \exp[b(-\gamma \phi H - \phi_{os}^* + \phi_{ref.})] \]  \hfill (A1.5)

The chemical dissolution reaction is given by

\[ \frac{dL}{dt} = \Omega_2 k_5^* C_H^n \]  \hfill (A1.6)

Equilibrium occurs when the film growth, eq. A1.3, is equal to the dissolution rate according to eq. A1.6. So one finds

\[ \exp(-b\epsilon L) = \frac{k_5^* C_H^n - k_{10}^* \exp(\alpha bE)}{k_2^* \exp[b(1-\alpha)E]} \]  \hfill (A1.7)

or equivalently:

\[ \exp(-b\epsilon L) = \frac{k_5^* C_H^n}{k_2^*} \exp[-(1-\alpha)bE] - \frac{k_{10}^*}{k_2^*} \exp[(2\alpha - 1)bE] \]  \hfill (A1.8)

When the film growth at the O/S interface is neglected, the film thickness increases linearly with the externally applied potential:

\[ \exp(-b\epsilon L) = \frac{k_5^* C_H^n}{k_2^*} \exp[-(1-\alpha)bE] \]  \hfill (A1.9)

\[ L = \frac{(1-\alpha)}{\epsilon} (E - E^*) \]  \hfill (A1.10)

where

\[ E^* = \frac{\ln(k_5^* C_H^n) - \ln(k_2^*)}{(1-\alpha)b\epsilon} \]  \hfill (A1.11)

It should be noted that the potential dependence of the thickness is in approximation linear for the case that also film growth occurs at the O/S interface.
Appendix 2  Potential and pH dependence of the components of the equivalent circuit.

The potential dependence of the equations 4.59 to 4.62 are evaluated in this appendix. The charge transfer resistance at the O/S interface and the parameters A, B and D of the inductive loop will be evaluated.

\[
\frac{1}{R_{os}} = \left\{3k_3b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}k_8b_8C_0\theta_{ao}\beta\right\}\alpha 
\]

(4.59)

\[
A = \left(3k_3 - \frac{4}{3}k_8C_0\beta\right)k_8b_8C_0\theta_{ao}\beta\alpha 
\]

(4.60)

\[
B = k_7 + k_{-7}C_H^2 + k_8C_0\beta 
\]

(4.61)

\[
D = \beta 
\]

(4.62)

**Evaluation of the potential dependence of \(R_{os}\)**

Applying eq. 4.64 to eq. 4.59 yields

\[
\frac{1}{R_{os}} = 3\alpha k_3b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}\alpha k_2b_8 
\]

(A2.1)

The parameter \(\alpha\) is quite small, which results in \(k_i = k_i^*(1+\alpha b_3E)\). Eq. A2.1 becomes:

\[
\frac{1}{R_{os}} = 3\alpha k_3^*(1+\alpha b_3E)b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}\alpha k_2b_8 
\]

(A2.2)

This results in:

\[
\frac{1}{R_{os}} = 3\alpha^2k_3^*b_3^2(1-\theta_{ao}-\theta_{aa})E + 3\alpha k_3^*b_3(1-\theta_{ao}-\theta_{aa}) + \frac{4}{3}\alpha k_2b_8 
\]

(A2.3)

For the potential dependence of \(R_{ad}\) and \(L_{ad}\) the parameters A, B and D are evaluated.
• Evaluation of the potential dependence of parameter A

\[ A = \left(3k_3 - \frac{4}{3}k_bC_\beta\right)k_bC_\beta \theta_{ao} \beta \alpha \]  
\[ (4.60) \]

applying eq. 4.64 yields:

\[ A = \left(3k_3 - \frac{4}{3}k_2 \theta_{oa}\right)k_2b_8\alpha \]  
\[ (A2.4) \]

\[ A = 3k_3^*(1 + \alpha b_3E)k_2b_8\alpha - \frac{4}{3} \frac{k_2^2b_8\alpha}{\theta_{oa}} \]  
\[ (A2.5) \]

\[ A = 3k_3^*k_2b_3b_8\alpha^2E + 3k_3^*k_2b_8\alpha - \frac{4}{3} \frac{k_2^2b_8\alpha}{\theta_{oa}} \]  
\[ (A2.6) \]

• Evaluation of the potential dependence of parameter B

\[ B = k_7 + k_{-7}C_{\beta}^2 + k_bC_\beta \beta \]  
\[ (4.61) \]

applying eq. 4.64 yields:

\[ B = k_7 + k_{-7}C_{\beta}^2 + \frac{k_2}{\theta_{oa}} \]  
\[ (A2.7) \]

The inductance \( L_{ad} \) and resistance \( R_{ad} \) are defined as:

\[ \frac{1}{R_{ad}} = \frac{A}{B} \]  
\[ (A2.8) \]

\[ \frac{1}{L_{ad}} = \frac{A}{D} \]  
\[ (A2.9) \]

Combination of eqs. 4.62, A2.6, A2.7 A2.8 and A2.9 yields
\[
\frac{1}{R_{ad}} = \frac{3k_3^2k_2b_3^2\alpha^2E + 3k_3^2k_2b_8\alpha - \frac{4}{3}k_2^2b_8\alpha}{k_7 + k_7\beta c_{H}^2 + \frac{k_2}{\theta_{oa}}} \quad (A2.10)
\]

\[
\frac{1}{L_{ad}} = \frac{\frac{3k_3^2k_2b_3^2\alpha^2E + 3k_3^2k_2b_8\alpha - \frac{4}{3}k_2^2b_8\alpha}{\beta}}{\theta_{oa}} \quad (A2.11)
\]

\[
\frac{1}{R_{os}} = 3\alpha^2k_3^2b_3^2(1 - \theta_{ao} - \theta_{aa})E + 3\alpha k_3^2b_3(1 - \theta_{ao} - \theta_{aa}) + \frac{4}{3}\alpha k_2b_8 \quad (A2.3)
\]

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IV PERMEATION STUDIES
5.1 Introduction
The study of water permeation in coatings is of great practical interest, in particular for the performance of coatings. From the discussion in chapter 2 it became clear that, as a result of diffusion, water may be present at the metal-coating interface. Hence water may lead there to wet-adhesion phenomena and subsequently to the initiation of corrosion processes. Nowadays capacitance measurements are the favoured technique to monitor the permeation process\textsuperscript{1-21}. The reason is that capacitance measurements are quite sensitive to the water content in the coating and can be performed with high accuracy. Another important reason is that the measurements can be performed in situ and are relatively easy to carry out.

The penetration rate of water into a coating is determined by several factors like the polymer composition and network structure\textsuperscript{17,23}. There are different modes of water transport in the polymer, depending on the factors mentioned above\textsuperscript{22-24}. The first is diffusion which is the result of a concentration gradient. Pseudo-Fickian diffusion is a special case which is characterised by an initial $\sqrt{t}$ increase of the absorbed weight but after a certain time a clear deviation from the $\sqrt{t}$ increase is observed. The second mode concerns water uptake which is controlled by polymer relaxation. In this case penetration of water in the polymer requires the movement of polymer chains to create space for the water molecule. When the polymer chain relaxation is fast compared to diffusion ideal-Fickian diffusion is observed, resulting in a $\sqrt{t}$ increase of the absorbed weight. This usually occurs in coatings above their glass transition temperature. When the diffusion rate the relaxation rate considerably exceeds, the permeation process is controlled by the relaxation process. This process is characterised by a typical time constant $\tau$ and consequently the absorbed weight increases linearly with $t$.

Finally other permeation modes where the relaxation and diffusion rates are of the same order, are called anomalous, or non-Fickian diffusion. This is often found in
polymer coatings in their glassy state. For most polymers the diffusion coefficient generally increases with the water concentration.

In this chapter water permeation measurements (i.e. accurate capacitance measurements) are reported which have been performed on eight coatings below the glass transition temperature. It is shown that the absorption curves deviate from ideal-Fickian diffusion. No unambiguous value for the diffusion coefficient can be determined. For all coatings the analysis points into the direction of pseudo-Fickian diffusion. To examine this further a new method of analysis is developed. Deviations from ideal-Fickian diffusion are mapped onto a time dependent diffusion rate. Applying this transformation to our measurement data it is found that for all our samples the diffusion rate decreases considerably in time. Remarkably the drop is almost uniform for the different types of coating, allowing us to construct an explicit model, valid for the eight coatings. An interesting property of a monotonically and smoothly decreasing diffusion rate is that it can be described equivalently in terms of a spectral distribution of diffusion rates. Applying this new perspective the width of the distribution is calculated and is shown to be a characteristic "diffusion" property of the coating.

It is shown that statistical effects, arising from local fluctuations in the coating properties, can in principle account for pseudo-Fickian behaviour. However, it is more probable that this response is the result of a relaxation process. The Berens-Hopfenberg relaxation model agrees well with our results. We show that this phenomenological model can be given a physical basis. It can be understood as a diffusion process, influenced by the redistribution of the free volume in the coating. The fact that water tends to cluster may prove to be responsible for this type of polymer rearrangement.

5.2 Experimental
The coatings have been applied to aluminium and steel panels, using the techniques listed in table 5.1.
The coated panels were stored at room temperature for at least two months to simulate ageing. Then a perspex tube was glued on the coating surface. Finally the panels were placed in an oven for at least 24 hours at 40°C to remove all water from the coating.
During the experiment the tube was filled with a 0.1 M NaCl solution which has a specific resistance of 100Ωcm. An electrode, a platinum grit with an exposed area of 10 cm², was put in the solution. The temperature during the measurements was kept constant at 22°C. This temperature is well below the glass transition temperature of the coatings. Hence the (crosslinked) polymers are in the glassy state. The specific resistance of the coatings is larger than 10¹⁰Ωcm, even after several months of exposure.

Capacitance measurements were used to monitor the water absorption in the coating. The measurements were performed with an Andeen-Hagerling ultra precision capacitance bridge, model 2500A and with an impedance measurement set, consisting of a Schlumberger Frequency Response Analyser (FRA), model 1255, and an Electrochemical interface (ECI), model 1286.

<table>
<thead>
<tr>
<th>coating type</th>
<th>coating</th>
<th>coating thickness</th>
<th>substrate</th>
<th>application technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>I epoxy</td>
<td>Epikote 862 (Shell) cured with Eurodure 43 (Schering). ¹⁶</td>
<td>88 ± 5 μm</td>
<td>mild steel (Q-panel company)</td>
<td>bar coater technique</td>
</tr>
<tr>
<td>II epoxy</td>
<td>Epikote 1001 (Shell) cured with Versamid 115. ¹⁷</td>
<td>53 ± 3μm</td>
<td>mild steel (Q-panel company)</td>
<td>sprayed</td>
</tr>
<tr>
<td>III polyurethane</td>
<td>supplied by Shell Research.</td>
<td>20 ± 2 μm</td>
<td>mild steel (Q-panel company)</td>
<td>c.e.d. process</td>
</tr>
<tr>
<td>IV polyurethane</td>
<td>supplied by Akzo coatings</td>
<td>22 ± 2 μm</td>
<td>Al 2024 T3 Clad</td>
<td>sprayed</td>
</tr>
<tr>
<td>V alkyd</td>
<td>supplied by T.N.O. cured at 50 °C for at least 60 hours</td>
<td>48 ± 3 μm</td>
<td>Al 3003 and HD 5050 alloys, grit 1200</td>
<td>bar coater technique</td>
</tr>
<tr>
<td>VI powder coating</td>
<td>supplied by V.O.M. ¹⁶</td>
<td>88 ± 3 μm</td>
<td>Al 6063 alloy</td>
<td>sprayed</td>
</tr>
<tr>
<td>VIII polyester</td>
<td>supplied by V.O.M. ¹⁶</td>
<td>146 ± 5 μm</td>
<td>Al 6063 alloy</td>
<td>sprayed</td>
</tr>
</tbody>
</table>

Table 5.1 Sample specifications
For the ac signal a frequency of 1 kHz and an amplitude of 125 mV were used. The dc potential was 0 mV. The accuracy of each measurement was about $10^{-3}$%.

5.3 Capacitance measurements
In impedance measurements an ac perturbation voltage, $V(\omega)$, is applied to the measurement cell, generating a current with the same angular frequency $I(\omega)$. The complex impedance $Z(\omega)$, defined as the ratio of applied voltage over current, characterises the response of the system.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$  \hspace{1cm} (5.1)

For coatings immersed in water the real part of the impedance is quite small at medium frequencies. The imaginary part can be written in terms of a capacitance $C$

$$\text{Im}Z(\omega) = -\frac{1}{\omega C}$$  \hspace{1cm} (5.2)

The capacitance has only an implicit frequency dependence. Since both the metal substrate and the electrolyte solution are highly conducting only the properties of the coating contribute to the capacitance. In fact the capacitance is directly proportional to the (frequency dependent) relative dielectric constant of the coating.

$$C = Q\varepsilon$$  \hspace{1cm} (5.3)

For an ideal capacitor the parameter $Q$ is proportional to the surface area $A$ of the electrode and inversely proportional to the coating thickness $L$

$$Q = \frac{A}{L}\varepsilon_0$$  \hspace{1cm} (5.4)

where $\varepsilon_0$ is the dielectric permittivity of vacuum. In practice $Q$ will also depend on other factors such as the geometry of the measurement cell. The thickness
dependence of eq. 5.4, however, is well confirmed by capacitance measurements both on dry and saturated coatings\textsuperscript{3,4,19}.

After immersion of the sample water permeates slowly into the coating. The result is a gradual increase of the relative dielectric constant of the coating and hence of the capacitance as a function of time. This is caused by the fact that the relative dielectric constant of water is much larger than that of the dry coating. Figure 5.1 shows a typical capacitance curve. From this figure it is observed that the capacitance increases monotonically from the value for the dry coating, $C_0 = C(0)$, to the saturation value, $C_S = C(\infty)$.

![Capacitance curve over time](image)

*Figure 5.1 Typical increase of coating capacitance as a function of time for a polyurethane coating (III), see table 5.1.*

To describe capacitance measurements on immersed coatings clearly two models are required. The first model describes the permeation of water into the coating and the second one the increase of the dielectric constant as a function of the water content, i.e.

\[ C(t) = Q_0 \varepsilon(\phi(t)) \]  \hspace{1cm} (5.5)

where $\phi$ is the volume fraction of water in the coating. As demonstrated in the next section the capacitance is not very sensitive to the choice of the second model.
5.4 Effective medium theories

It is generally assumed that water permeating into a coating occupies the free volume of the polymer chains. As a function of time, the volume fraction water increases and the volume fraction vacuum decreases. The coating can therefore be considered as a mixture of polymer, water and vacuum. The relative dielectric constants of these three media are quite different. The dielectric constant of free space (vacuum) is by definition equal to unity. From measurements on dry coatings one finds with eqs 5.3 and 5.4 that the dielectric constant of the coating is in the range of 3 to 5. Consequently polymers must have roughly the same value. The low frequency value for the relative dielectric constant of (free) water is 80. For water molecules absorbed in a coating the value is not well-known since they can be adsorbed at certain sites of the polymer chain. The relative dielectric constant of water in a polymer is usually assumed to be in the range of 50 to 80.

In the calculations in this chapter the following values for the different dielectric constants have been used: $\varepsilon_v=1$, $\varepsilon_p=3$ and $\varepsilon_w=80$.

For mixtures the dielectric constant $\varepsilon$ is described by an effective medium theory. Most models for $\varepsilon$ can be represented in the following form:

$$f(\varepsilon) = \sum_n \phi_n f(\varepsilon_n)$$  \hspace{2cm} (5.6)

where $f$ is the function characterising the mixing law, the $\phi_n$ are the volume fractions of the different materials satisfying $\sum_n \phi_n = 1$ and $\varepsilon_n$ the relative dielectric constants of the components.

The appropriate choice of the function $f$ is determined by the geometry of the system. For example for a stratified material the solutions for parallel and perpendicular external electric fields can be presented in the form of eq. 5.6 with the following function

parallel: $f(\varepsilon) = \varepsilon$ \hspace{2cm} (5.7)

perpendicular: $f(\varepsilon) = 1/\varepsilon$ \hspace{2cm} (5.8)

For isotropic media several choices of the function $f$ are in use. The following four most commonly used in the field of water absorbing systems are applied in the
calculations in this chapter. For dielectric systems Looyenga and Brasher have proposed simple empirical mixing laws where the link to geometry is not clear\(^2\).

**Brasher:**
\[ f(\varepsilon) = \log(\varepsilon) \]  \hspace{1cm} (5.9)

**Looyenga:**
\[ f(\varepsilon) = \varepsilon^{1/3} \]  \hspace{1cm} (5.10)

More sophisticated models, that can also describe the response of dissipative (complex \(\varepsilon\)) systems, are based on the polarizability of spherical inclusions. The function \(f\) then takes the following form

\[ f(\varepsilon) = \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \]  \hspace{1cm} (5.11)

where \(\varepsilon_m\) is the (fictitious) relative dielectric constant of the embedding medium. Two different choices for \(\varepsilon_m\) are used. First of all one of the components can take the role of the embedding medium [Rayleigh, Maxwell-Garnett, Clausius-Mosotti, Lorentz-Lorenz]. For a coating the correct choice for the host material appears to be the polymer, so one has to set \(\varepsilon_m = \varepsilon_p\) in eq. 5.11.

Secondly for some mixtures none of the components clearly acts as a the host material. Then the symmetric choice \(\varepsilon_m = \bar{\varepsilon}\) is appropriate. This is called the Effective Medium Approximation [Bruggeman, Böttcher]. Note that for a three phase system \(\bar{\varepsilon}\) is the solution of a third order equation.

From the ratio of the capacitances of the saturated and dry coating, respectively \(C_s\) and \(C_o\), one can now calculate \(\phi_s\), the maximum volume fraction of water in the coating. This value depends on the effective medium theory chosen. So in principle if \(\phi_s\) is known (e.g. determined by an accurate gravimetric measurement) the correct effective medium theory can be deduced. In practice this is not realistic since only the order of magnitude of \(\phi_s\) is known. In fact it is customary to apply different effective medium theories to examine the range of typical \(\phi_s\) values. In table 5.2 the results are shown for our coatings.
<table>
<thead>
<tr>
<th>coating type</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{C_s}{C_o} - 1 )</td>
<td>0.140</td>
<td>0.075</td>
<td>0.148</td>
<td>0.144</td>
<td>0.180</td>
<td>0.110</td>
<td>0.253</td>
<td>0.074</td>
</tr>
<tr>
<td>Looyenga</td>
<td>1.93</td>
<td>1.06</td>
<td>2.04</td>
<td>1.99</td>
<td>2.45</td>
<td>1.54</td>
<td>3.37</td>
<td>1.05</td>
</tr>
<tr>
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<td>1.65</td>
<td>3.15</td>
<td>3.07</td>
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<td>2.38</td>
<td>5.15</td>
<td>1.64</td>
</tr>
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<td>3.76</td>
<td>3.66</td>
<td>4.47</td>
<td>2.86</td>
<td>6.00</td>
<td>1.98</td>
</tr>
<tr>
<td>Rayleigh</td>
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<td>2.05</td>
<td>3.94</td>
<td>3.84</td>
<td>4.73</td>
<td>2.97</td>
<td>6.48</td>
<td>2.03</td>
</tr>
</tbody>
</table>

*Table 5.2* \( \phi_s \) in (%) calculated with 4 effective medium theories for the different coatings

Once an effective medium theory is chosen the value of \( \phi_s \) can be computed from \( C_s/C_o \) as in table 5.2, and similarly \( \phi(t) \) from \( C(t)/C_o \). It is now convenient to introduce the reduced volume fraction \( \psi(t) \).

\[
\psi(t) = \frac{\phi(t)}{\phi_s}
\]  

(5.12)

\( \psi(t) \) is also known as the saturation function, since it increases monotonically from 0 at \( t=0 \) to 1 at \( t=\infty \). Importantly the choice of the effective medium theory and even the precise values of the different dielectric constants have little effect on \( \psi(t) \). We demonstrate this in two ways.

First of all the fact that \( \phi_s \) is small (see table 5.2) can be used. Expanding the capacitance up to second order in the volume fraction yields

\[
\frac{C(\phi(t)) - C_o}{C_s - C_o} = \frac{\varepsilon(\phi(t)) - \varepsilon(0)}{\varepsilon(\phi_s) - \varepsilon(0)} \equiv \psi(t) \left\{ 1 - \frac{1}{2} \phi_s (1 - \psi(t)) \frac{\varepsilon''(0)}{\varepsilon'(0)} \right\}
\]

(5.13)

where a prime denotes differentiation. From the fact that \( \phi_s \) is small it follows that the second term on the right hand side of eq. 5.13, describing the influence of the effective medium theory, has only a marginal influence.

An alternative approach is to consider the coating as a two-layer system. Absorbed water is only present in the top layer of thickness \( L \psi(t) \). This layer is saturated with water. The bottom layer of thickness \( L(1-\psi(t)) \) is dry. The diffusion front slowly moves across the coating until it reaches the coating-substrate
The coating is then fully saturated. In appendix 1 it is shown that, by applying eq. 5.8, the following relation holds for this model

\[
\frac{1/C(\phi(t)) - 1/C_0}{1/C_s - 1/C_0} = \psi(t) \tag{5.14}
\]

Interestingly this result is completely independent of the dielectric constants and of the effective medium theory chosen for the wet and dry layer.

Both eqs. 5.13 and 5.14 demonstrate clearly that the time dependence of the capacitance is dominated by the permeation process. The conversion of the capacitance \(C(t)\) to the saturation function \(\psi(t)\) is straightforward.

5.5 Water permeation: ideal-Fickian diffusion

The permeation of water in a coating is caused by diffusion, a process governed by several different factors. In this section we restrict ourselves to the simplest case, ideal Fickian diffusion. Ficks law for one-dimensional diffusion is

\[
\frac{\partial c(z,t)}{\partial t} = D \frac{\partial^2 c(z,t)}{\partial z^2} \tag{5.15}
\]

where \(c\) is the concentration of water and \(D\) the diffusion coefficient which is assumed to be constant. Typically \(D\) is of the order of \(10^{-13}\) m\(^2\)s\(^{-1}\) as reported in literature\(^1,8,9,16,17,19-21,23\). The appropriate boundary conditions for a submersed coating are

\[
c(z,0) = 0, \quad c(0,t) = c, \quad \frac{\partial c}{\partial z}(L,t) = 0 \tag{5.16}
\]

For the full solution of eqs. 5.15 and 5.16 we refer to the textbooks\(^22-24\). The saturation function \(\psi(t)\), also known as the fractional mass uptake \(M/M_\infty\), can be identified with the scaled average water concentration. To distinguish the actual saturation function from the model solution for ideal-Fickian diffusion we denote the latter by \(\psi_o\). It is given by\(^22-24\)

\[
\psi_o(x) = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 x}{4}\right) \tag{5.17}
\]
where $x$ is a dimensionless time defined by

$$x = \frac{t}{\tau}$$  \hspace{1cm} (5.18)

The parameter $\tau$ determines the time scale of the diffusion process

$$\tau = \frac{L^2}{D}$$  \hspace{1cm} (5.19)

Two approximations of eq. 5.17 are very convenient. For small values of $x$ (short times) the summation can be replaced by an integration, yielding

$$\psi_o(x) \equiv \frac{2}{\sqrt{\pi}} \sqrt{x}$$  \hspace{1cm} (5.20)

In the long time limit it is sufficient to retain only the $n=0$ term in eq. 5.17, giving

$$\psi_o(x) \equiv 1 - \frac{8}{\pi^2} \exp \left( -\frac{\pi^2}{4} x \right)$$  \hspace{1cm} (5.21)

These asymptotic expressions are very accurate. With an error of less than 0.001 eq. 5.20 is valid for $\psi_o < 0.52$ ($x < 0.21$) and eq. 5.21 for $\psi_o > 0.52$ ($x > 0.21$). So, no transition region between the short and long time region is present.

It should be stressed that eq. 5.17 is an idealisation of the diffusion process that applies to only a limited number of systems. In section 5.7 a method is introduced that allows one to incorporate deviations from ideal-Fickian diffusion into eq. 5.17.

### 5.6 Asymptotic methods

Measurements of water absorption in coatings are often analysed using the asymptotic expressions, eqs. 5.20 and 5.21, derived for ideal-Fickian diffusion. Such a method is convenient in those cases where one is satisfied with a rough estimate of the diffusion coefficient. Alternatively, the asymptotic methods can be regarded as a preliminary investigation of the data. The motivation is that these
methods are quite easy to apply and indicate directly whether the assumption of ideal-Fickian diffusion is valid.

First of all $C_o$ and $C_s$ have to be estimated for the different coatings. Then the capacitances are converted to the saturation function. To this end the effective medium theories mentioned in section 5.4 or the two-layer model, eq. 5.14, may be used. In practice Brashers mixing law is mostly used. The volume fraction is then given by

$$\phi(t) = \frac{\log \left( \frac{C(t)}{C_o} \right)}{\log \left( \frac{e_w}{e_v} \right)}$$

(5.22)

and the saturation function $\psi(t)$ by

$$\psi(t) = \frac{\phi(t)}{\phi_s} = \frac{\log \left( \frac{C(t)}{C_o} \right)}{\log \left( \frac{C_s}{C_o} \right)}$$

(5.23)

For short times eqs. 5.18 and 5.20 predict a $\sqrt{t}$-dependence of $\psi(t)$. From a plot of $\psi(t)$ versus $\sqrt{t}$ the parameter $\tau$ and with eq. 5.19 the diffusion coefficient can be determined. For all our coatings the $\sqrt{t}$ dependence was well confirmed.

![Figure 5.2 Typical plot of $\psi(t)$ for a polyurethane coating (III). solid line is the ideal-Fickian solution.](image-url)
Figure 5.2 shows a typical plot. Also shown is the curve for ideal-Fickian diffusion, eq. 5.17, where the linear relationship between $\psi$ and $\sqrt{t}$ holds over a longer time region. In the long time limit $1 - \psi(t)$ must be considered. From eq. 5.23 one finds

$$1 - \psi(t) = \log\left(\frac{C_s}{C(t)}\right) \log\left(\frac{C_s}{C_0}\right)$$

(5.24)

The asymptotic expression for ideal diffusion, eq. 5.21, can be rewritten as

$$-\left(\frac{4}{\pi^2}\right)\log\left(\frac{\pi^2}{8}(1 - \psi(t))\right) = \frac{t}{\tau}$$

(5.25)

So a plot of the left hand side of eq. 5.25 versus time should produce a curve, that approaches a straight line through the origin for long times. An example is given in figure 5.3. For all our coatings a linear relationship is indeed found over a very wide time region. This confirms the exponential law for the saturation function at long times. For some coatings deviations occur at very long times, indicating the onset of non-diffusional processes. The value of $\tau$ is considerably larger than that obtained from the short time fit. The ratio is in the range of 1.4 to 9. Also the asymptote is not a line through the origin but intersects the positive y-axis.

![Graph](image)

*Figure 5.3  The long time behaviour of the polyurethane coating (III)*

From the application of the asymptotic methods based on ideal-Fickian diffusion the following conclusions can be drawn, valid for the eight coatings:
• Both the $\sqrt{t}$-dependence for short times and the exponential law for long times are well confirmed.
• The linear relationship between $\psi(t)$ and $\sqrt{t}$ is valid over a shorter time region than predicted by eq. 5.17.
• The diffusion coefficients calculated from the short and long time behaviour do not match. The second one is consistently found to be smaller.
• The asymptotic line in the plot based on the long time behaviour deviates from eq. 5.25 since it intersects the y-axis at a positive value.

From the analysis in this paragraph it follows that ideal-Fickian diffusion, which assumes that the diffusion process can be described by a constant diffusion coefficient, here leads to inconsistent results. In particular the third point, the different values found for the diffusion coefficient at short and long times, is conclusive. This result has been observed for water permeation in glassy polymers by several authors\textsuperscript{1,6,7,21,33,34}. In fact from the above results it follows that the water permeation is described by a pseudo-Fickian diffusion process\textsuperscript{25}. To examine this further a more sophisticated method of analysis is developed in section 5.7 and applied to our measurements in section 5.8.

5.7 Transformation to a time dependent diffusion rate
In the previous section it has been demonstrated that the asymptotic methods, when applied to non-ideal diffusion, are of limited value. In this section we introduce a new approach. It also takes ideal diffusion as a starting point. However, this method is valid over the entire time region since it uses the full solution, eq. 5.17, in stead of the asymptotic expressions, eqs. 5.20. and 5.21. This way deviations from ideal-Fickian diffusion can be analysed more fundamentally. More importantly the method allows one to incorporate observed deviations into the model. Thus an improved diffusion model is obtained.

As before, the values of $C_0$ and $C_s$, the capacitances of the dry and saturated coating, have to be estimated. The saturation function $\psi(t)$ can then be calculated using an appropriate effective medium theory. Now the actual saturation function is equated to the solution of ideal-Fickian diffusion, eq 5.17.

$$\psi_0(x) = \psi(t) \quad (5.26)$$
This is equivalent to

\[ x = \psi_0^{-1}(\psi(t)) \quad (5.27) \]

Here, \( \psi_0^{-1} \) is the inverse of the function \( \psi_0 \) which can be evaluated numerically without difficulty. Eq. 5.27 relates the actual time \( t \) involved in the diffusion process to a dimensionless time \( x \) for ideal-Fickian diffusion. Clearly, if \( \psi(t) \) is correctly described by ideal-Fickian diffusion, then from the definition eq. 5.18 it follows that the dimensionless time \( x \) is simply proportional to \( t \),

\[ x(t) = \frac{t}{\tau} \quad (5.28) \]

where \( 1/\tau \) is the (constant) diffusion rate of ideal diffusion. In general diffusion is not ideal, meaning that the linear relationship between \( x \) and \( t \) of eq. 5.28 is not valid. Hence the diffusion rate \( 1/\tau \) must be considered time dependent. The obvious generalisation of eq. 5.28 is

\[ x(t) = \int_0^t \frac{1}{\tau(t')} dt' \quad (5.29) \]

The validity of eq. 5.29 can be verified by solving Ficks equation for one-dimensional diffusion, eq. 5.15, where the diffusion coefficient now has an explicit time dependence. It follows that the time dependent diffusion rate \( 1/\tau(t) \) can be obtained from \( x(t) \) by taking the derivative with respect to time

\[ \frac{1}{\tau(t)} = \frac{\partial x(t)}{\partial t} \quad (5.30) \]

The purpose of the transformations \( C(t) \to \psi(t) \to x(t) \to 1/\tau(t) \) is now explained. It is well-known that for different permeation processes the corresponding \( C(t) \) or \( \psi(t) \) curves are closely similar. The transformation to \( x(t) \) and in particular to \( 1/\tau(t) \) enhances the details of the original curves, in particular deviations from Fickian behaviour. Analysis of the \( 1/\tau(t) \) curve enables one to construct a suitable model for a time dependent diffusion rate. Substitution of this expression into eq. 5.29 yields \( x(t) \) and finally an improved model for \( \psi(t) \) is obtained from eq. 5.26. Figure 5.4 shows schematically the purpose of the transformations.
5.8 Application of the 1/τ(t)-approach to the measurements

In accordance with the method outlined in section 5.7 the saturation function for the different coatings using \( C_o \) and \( C_s \) and Brashers mixing law, eq. 5.23 have been determined. Next \( x(t) \) has been calculated using eq 5.29. Finally 1/τ(t) is obtained from eq. 5.30 in combination with a smoothing procedure. Figure 5.5 shows a typical 1/τ(t)-plot and figure 5.6 the corresponding \( x(t) \)-plot.

![Graph showing 1/τ(t) for a polyurethane coating](image)

**Figure 5.5 1/τ(t)-plot for a polyurethane coating (III).**

At short times (typically \( \psi(t) < 0.4 \)) 1/τ is practically constant. Then it is consistently found that at intermediate times (0.4 < \( \psi(t) < 0.8 \)) a considerable decrease occurs. For long times (\( \psi(t) > 0.8 \)) 1/τ becomes nearly constant. For very long times the time dependence is rather unclear, and in fact it is different for each coating. One reason is that the plot becomes increasingly sensitive to the precise value of \( C_s \).
and to noise in the data. Another reason is that, due to the very long immersion time, processes other than diffusion may start interfering.

![Graph](image)

**Figure 5.6 Typical x(t)-plot for a polyurethane coating (III).**

Figure 5.6 shows a typical $x(t)$ plot. The flattening of the $x(t)$-curve and the linear regimes for both short and long times are very characteristic. From the analysis of the different $x(t)$ and $1/\tau(t)$ curves it is concluded that at short times $x(t)$ is well approximated by

$$x(t) = \frac{t}{\tau_0} \quad (5.31)$$

where the parameter $1/\tau_0$ describes the diffusion rate at short times. For long times a different linear relationship between $x$ and $t$ holds.

$$x(t) = x_0 + \frac{t}{\tau_s} \quad (5.32)$$

where $\tau_s$ is a characteristic time scale which is consistently found to be larger than $\tau_0$. This confirms the result of the asymptotic methods of section 5.6. $x_0$ is a positive constant, describing the time difference between the actual and apparent time involved in the diffusion process. From eq. 5.29 one has

$$x_0 = \int_0^\infty \left\{ \frac{1}{\tau(t') - \tau_s} \right\} dt' \quad (5.33)$$
It follows that the parameter $x_0$ is a direct result of the drop in the diffusion rate and is closely related to $\tau_0$ and $\tau_s$. As noted above the response at very long times is not quite clear. It is assumed that it is also well described by eq. 8.2. On the basis of the asymptotic expressions eqs. 5.31 and 5.32 an expression for $x(t)$ can be constructed which is valid for the entire time region.

$$x(t) = \frac{t}{\tau_s} + x_0 \{1 - F(t)\} \tag{5.34}$$

The function $F(t)$ describes the transition from the short time to the long time behaviour. Numerical tests show that for all coatings the function $F(t)$ can be well represented by the following expression:

$$F(t) = 2 / \left[1 + \alpha t + \frac{3}{2} (\alpha t)^2 + \frac{1}{12} (\alpha t)^3 + \exp(\alpha t)\right] \tag{5.35}$$

where $\alpha$ is given by

$$\alpha = \frac{1}{x_0} \left(\frac{1}{\tau_0} - \frac{1}{\tau_s}\right) \tag{5.36}$$

All capacitance measurements have been analysed with this new pseudo-Fickian diffusion model. The least squares fitting routine used was an iterative procedure based on steepest descent with curvature correction. The fit involves 5 parameters: $Q$, $\phi_s$, $\tau_0$, $\tau_s$ and $x_0$. The first two determine $C_0$ and $C_s$, the latter three the shape of the $C(t)$ curve. Table 5.3 shows the results. Also shown are the results for the ideal diffusion model, a three parameter fit ($Q$, $\phi_s$, $\tau$). As a measure of the quality of the fit the scaled rms error per data point, denoted by $\Delta$, has been calculated.

$$\Delta = \frac{1}{(C_s - C_0)} \left\{ \frac{1}{N} \sum_{i=1}^{N} (C_i - \tilde{C}_i)^2 \right\}^{1/2} \tag{5.37}$$

where $C_i$ is the measured value of the capacitance and $\tilde{C}_i$ the model prediction. Clearly the reduction in the rms error per data point is considerable, of the order 10. For coating I the values of $\tau_0$ and $\tau_s$ differ not much, and the improvement of the fit is rather small, a factor 2.3. For coating V however the ratio of $\tau_s$ over $\tau_0$ is
large, a factor 9. It is not surprising that the description in terms of ideal-Fickian diffusion fails. The improvement in the fit is here enormous, a factor 51!

<table>
<thead>
<tr>
<th>coating type</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>523</td>
<td>560</td>
<td>52</td>
<td>23</td>
<td>66</td>
<td>171</td>
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<td>787</td>
</tr>
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<td>24.9</td>
<td>16.1</td>
<td>30.4</td>
<td>21.0</td>
<td>16.5</td>
<td>26.0</td>
</tr>
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<td>18</td>
<td>44</td>
<td>111</td>
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<td>751</td>
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<td>46</td>
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<td>0.6</td>
<td>2.0</td>
<td>7.5</td>
<td>9.0</td>
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</table>

*Table 5.3 Parameter values and rms values for ideal (I) and pseudo (P) - Fickian diffusion.*

To check whether F(t) is indeed not a function of the effective medium theory and describes only the diffusion model, the measurement data were analysed using different effective medium theories. The parameter σ, which is a measure for the distribution of the τ's (see next section) and the rms error, listed in table 5.4, are constant, indicating the expected independence on the choice of the effective medium theory.

<table>
<thead>
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</tr>
<tr>
<td>µ</td>
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<td>Two Layer</td>
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*Table 5.4 Parameter values and rms values for different effective medium theories.*

5.9 **Interpretation in terms of a spectral distribution.**

In the previous section it is shown that pseudo-Fickian diffusion in glassy polymers can be described by a monotonically decreasing diffusion rate (see fig. 5.5). One may demonstrate that ψ(t) can then also be represented in terms of a spectral distribution, provided that the drop is sufficiently smooth as a function of
time. Numerical tests indicate that the function \( F(t) \), eq. 5.35, satisfies this criterion. We can then write

\[
\psi(t) = \int_0^\infty \rho(\tau)\psi_o(t / \tau) d\tau
\]

(5.38)

where \( \rho \) is a normalised distribution function, i.e.

\[
\int_0^\infty \rho(\tau) d\tau = 1
\]

(5.39)

The physical interpretation of eq. 5.38 is that the diffusion process can no longer be described by a single constant diffusion coefficient. Water permeation occurs simultaneously at different rates. The special case of ideal-Fickian diffusion now corresponds to a narrow spectral distribution, in the limiting case represented by a \( \delta \)-function. Let us consider the short time limit of diffusion as described by eq. 5.38. Substitution of the asymptotic expression, eq. 5.20, yields:

\[
\psi(t) = \frac{2\sqrt{t}}{\sqrt{\pi}} \int \rho(\tau)\tau^{-1/2} d\tau
\]

(5.40)

Eq. 5.40 is valid, provided the integral converges. In general this will be the case and hence the usual \( \sqrt{t} \) dependence is obtained. Comparing this result with eqs. 5.31 and 5.20 one sees that the integral in eq. 5.40 can then be identified with \( \tau_o^{-1/2} \). The long time behaviour is more complicated. With eq. 5.21 one finds

\[
\psi(t) = 1 - \frac{8}{\pi^2} \int \rho(\tau) \exp\left(\frac{\pi^2}{4} \frac{t}{\tau}\right) d\tau
\]

(5.41)

The time dependence which results from the integration is in general non-exponential. In section 5.6 and 5.8 however, we have seen that the long time limit is well described by an exponential law. From this one can conclude that the spectral distribution has no important contributions at very long times. The distribution must quickly drop to zero for \( \tau \) values larger than a certain \( \tau_{\text{max}} \).

Let us now construct the spectral distribution corresponding with the diffusion model derived in the previous paragraph. For simplicity we restrict ourselves to
the asymptotic behaviour, eqs. 5.31 and 5.32. Consider a $\rho(\tau)$ distribution with only two diffusion rates.

$$\rho(\tau) = A_1 \delta(\tau - \tau_1) + A_2 \delta(\tau - \tau_2)$$  \hspace{1cm} (5.42)

with $A_1 + A_2 = 1$ and $\tau_2 > \tau_1$. Substitution into eq. 5.38 yields

$$\psi(t) = A_1 \psi_0(t / \tau_1) + A_2 \psi_0(t / \tau_2)$$  \hspace{1cm} (5.43)

Using the short and long time limit of eq. 5.43 one can easily relate the three parameters $\tau_1$, $\tau_2$ and $A_1$ to the experimentally determined parameters $\tau_0$, $\tau_s$ and $x_0$. One finds

$$\tau_0 = \left( A_1 \tau_1^{-1/2} + A_2 \tau_2^{-1/2} \right)^2$$  \hspace{1cm} (5.44)

$$\tau_s = \tau_2$$  \hspace{1cm} (5.45)

$$x_0 = \frac{4}{\pi^2} \log(1 - A_1)$$  \hspace{1cm} (5.46)

It is interesting to consider the parameter $x_0$. In section 5.8 it described a time shift, related to the drop in the diffusion rate. According to eq. 5.46 a non zero value for $x_0$ results from the fact that a fraction $A_1$ of the diffusion process occurs at a fast rate and consequently does not contribute to diffusion in the long time limit. Hence $x_0$ can also be interpreted as a saturation effect.

With eqs. 5.44 to 5.46 the results of the previous section can be transformed into the spectral representation eq. 5.42. Note that this is an approximation since the function $F(t)$ does not appear. As a characteristic width of the spectrum the parameter $\sigma$ is defined as the standard deviation divided by the mean.

$$\sigma \equiv \frac{\left( \langle \tau^2 \rangle - \langle \tau \rangle^2 \right)^{1/2}}{\langle \tau \rangle}$$  \hspace{1cm} (5.47)

The parameter $\sigma$ is a dimensionless quantity that conveniently takes into account effects of the three parameters $\tau_0$, $\tau_s$ and $x_0$. In table 5.5 the results of this computation for all coatings are shown. Clearly the spectral width is quite large.
coating type
\[ \begin{array}{|c|c|c|c|c|c|}
\hline
& I & II & III & V & VI \\
\hline
\sigma & 0.32 & 0.81 & 0.72 & 1.27 & 0.83 \\
\Delta t / \Delta p & 2.3 & 16 & 16 & 51 & 11 \\
\hline
\end{array} \]

Table 5.5 Spectral width and fit improvement for coatings I, II, III, V and VI.

The spectral width \( \sigma \) is a measure for the magnitude of deviations from ideal-Fickian diffusion. This is well illustrated by table 5.5.

5.10 Physical interpretation
Diffusion is a process determined by many different factors. This is particularly true for the diffusion and sorption processes in glassy polymers. The relevant properties of a coating can be roughly divided into two categories. First of all there are structural factors resulting from local inhomogeneties, such as pores, microvoids etc. These are partly the result of the fabrication technique and partly related to the disordered nature of the glassy polymer. Secondly there are (thermo-)dynamical factors of the penetrant-polymer system. These include relaxation processes, mobilities of polymer chains and penetrant, stress, swelling etc. Over the last decades several mechanisms from both categories have been proposed to describe certain sorption anomalies. For some examples of non-Fickian behaviour, such as Case II diffusion and dual-mode sorption, satisfactory descriptions have been obtained. The origin of pseudo-Fickian behaviour however is as yet unclear. In the next section different approaches towards a modelling of pseudo-Fickian behaviour are discussed.

5.10.1 Structural effects
In this section the effects of the structural properties of a coating are discussed. These properties can influence the sorption in different ways. Neogi\(^{32}\) has considered the case where the number of defects per unit of volume is small. Classical Fickian diffusion in the coating then yields the main contribution to the sorption process. The defects absorb differently, thereby influencing slightly the concentration profiles. The result is a small modification of the sorption behaviour
and the diffusion rate. Neogi's calculations for spherical microvoids indicate that this model does not lead to pseudo-Fickian behaviour.

Another possibility is that the structural defects, due to their number, considerably affect the sorption behaviour. Then the statistical effects, resulting from differences in defect geometry and distribution, can be important and should be considered. This idea is supported by the previous section, where it was found that a spectral distribution of Fickian diffusion rates can account for pseudo-Fickian behaviour; in this interpretation diffusion takes place simultaneously at different rates. To examine the connection between fluctuations and the spectrum of diffusion rates, we construct a simple model for a coating, namely a parallel system of non-interacting cells. Each cell has a diffusion rate $\tau_i$ and an accessible volume $V_i$. The water content of the coating as a function of time is then given by

$$\psi(t) = \frac{\sum V_i \psi_0(t/\tau_i)}{\sum V_i}$$  \hspace{1cm} (5.48)

In the continuum limit the summation can be replaced by an integration, leading to eq. 5.38. Note that the accessible volume $V_i$ is then incorporated as a weight function in the $\rho(\tau)$ distribution. Since macroscopically the coating is homogeneous, it is clear that differences in the diffusion times $\tau_i$ of the cells must have their origin in statistical fluctuations of the properties of the polymer coating. This seems reasonable in view of the fact that glassy polymers are in an amorphous and disordered state.

A porous network model can take statistical effects of structural properties into account. Several studies (for references consult the review article of Saltzman\textsuperscript{27}) have been performed that relate transport properties in heterogeneous media to pore geometry. There is now consensus that pore geometry has a significant effect on properties such as permeation. Both the path length (tortuosity) and the time required to traverse a pore are known to be affected. It is known that the transit time in a pore element depends strongly on the geometry and in particular on the size of the exit\textsuperscript{27}. Bhatia\textsuperscript{28} analysed the effect of the pore dispersion parameter and found that it considerably effects the tortuosity. From the magnitude of this effect Bhatia concluded that diffusion in the narrower pores occurs at such a slow rate that their contribution is not important. Hence diffusion tends to occur along preferred paths.

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In a porous model approach the coating is assumed to be rigid. The mobility of the polymer chains is ignored. Alternatively one may attribute local fluctuations in diffusion rate to a thermo-dynamical origin, e.g. the activations energies$^{39,40}$ of the polymer chain and its side chains, or different mobilities of water in a polymer.

From the discussion above it is concluded that statistical effects can in principle account for pseudo-Fickian diffusion. However, there are substantial problems with this interpretation that should be considered. First of all the thickness of a coating is much larger than the dimensions of a polymer chain. Hence water molecules visit a large number of diffusion sites. Due to this averaging effect it is unclear whether large differences in $\tau_i$, corresponding with the broad spectrum found in the previous section, can be accounted for. Secondly, the idea of non-interacting cells is probably not very realistic. Transport between neighbouring cells will tend to smoothen existing concentration differences.

5.10.2 (thermo-) dynamical mechanisms
We now consider (thermo-) dynamical mechanisms and in particular relaxation processes. There is consensus in literature that relaxation, i.e. the rearrangement of the polymer chains in response to the penetrant, is an important mechanism. From the excellent review article of Frisch$^{25}$: "In glassy polymers, there appear to be significant contributions to transport processes from longer relaxation time parts of the characteristic spectrum of the polymer. In the presence of the penetrant motions of whole or portions of glassy polymer chains are not sufficiently rapid to completely homogenize the penetrant's environment." This view is shared by Rogers$^{29}$: "Deviations from Fickian behaviour generally arise as a consequence of the finite rates by which changes in polymer structure occur in response to stresses imposed upon the medium before and during the sorption-diffusion process."

For e.g. Case II diffusion relaxation models have indeed been successfully developed. According to Rogers$^{29}$ pseudo-Fickian behaviour may also be caused by relaxation: "In many cases, relatively long-term relaxation processes may delay the rate of approach to equilibrium with consequent marked effects on concurrent diffusion and sorption behaviour." Even so, the precise mechanism by which relaxation influences diffusion and sorption processes is not resolved. We shortly mention some of the ideas that have been proposed.
One idea is that the penetrant generates stress and swelling in the polymer. To account for this, the equation for the flux is modified by adding a stress contribution. The stress is assumed to relax with a typical time \( \tau_r \). Combining this with a diffusion coefficient that increases exponentially with concentration, Wu and Peppas were able to describe Case II diffusion and the transition from Case I to Case II quite well.

Another idea is that, since polymer chains have a limited mobility, concentration gradients do not contribute instantaneously to the flux. For this reason a relaxation time is incorporated in the expression for the flux. Numerical simulations confirm that this model also leads to Case II diffusion.

In fact it is not hard to understand that pseudo-Fickian behaviour can not be explained by the two above mentioned models. In a (Fickian) diffusion process concentration gradients and stresses are clearly most pronounced in the early stages. Hence the slow relaxation of these quantities has far more effect in slowing down diffusion at short times than at longer times. For pseudo-Fickian behaviour to occur the opposite should be true.

A third relaxation model has been proposed by Berens and Hopfenberg. In this phenomenological model the sorption is split into two contributions. One describes Fickian (fast) diffusion and the other sorption due to relaxation (slow). Applying this idea to a coating one obtains

\[
\psi(t) = A_D \psi_0 \left( t / \tau_D \right) + A_R \left( 1 - \exp(-t / \tau_R) \right)
\]

(5.49)

where \( \tau_D \) is the diffusion rate, \( \tau_R \) the first order relaxation rate, and \( A_D + A_R = 1 \). Note the strong similarity between this model, eq. 5.49, and the two \( \delta \)-function representation of our model eq. 5.43. Expressions like eq. 5.43 have been used to interpret various non-Fickian anomalies, such as sigmoidal and two-stage sorption. Importantly, for \( \tau_R \) sufficiently large compared to \( \tau_D \) eq. 5.49, in much the same way as eq. 5.43, predicts pseudo-Fickian behaviour. Then the model can be compared to the formula we derived in section 5.8. The three parameters \( \tau_D, \tau_R \) and \( A_R \) can be related quite easily to the parameters of our model \( \tau_0, \tau_s \) and \( x_0 \).

From the long time behaviour one finds

\[
\tau_s = \frac{\pi^2}{4} \tau_R
\]

(5.50)
\[ x_0 = -\left( \frac{4}{\pi^2} \right) \log \left( \frac{\pi^2}{8} A_R \right) \] (5.51)

Similarly one finds using the short time limit

\[ \tau_0 = A_D^2 \tau_D \] (5.52)

However, care must be taken since the two models differ somewhat at intermediate times. A considerable drop of the diffusion rate is predicted by both models, but in the Berens-Hopfenberg model this drop is preceded by an initial increase. It is therefore more appropriate to average the diffusion rates over the initial period and to identify \( \tau_0 \) with this value. The following modification of eq. 5.52 is found to be satisfactory

\[ \tau_0 = \tau_D \frac{1 - 0.67 A_D A_R}{A_D^2 + 0.52 A_D A_R (\tau_D / \tau_R)} \] (5.53)

To compare the two models, in figure 5.7 the two diffusion rates are plotted as a function of the saturation. The parameter values of coating III in table 3 were used. For the Berens-Hopfenberg model these were converted using eqs. 5.50, 5.51 and 5.53. One sees that the two models agree quite well about the three regimes: an initial region where the rate is relatively large, an intermediate region where the rate decreases and finally a region with a low sorption rate. Fickian diffusion characterises the response in the first region. In the Berens-Hopfenberg model the Fickian response is slightly affected by relaxation, so that the rate increases with \( \sqrt{t} \). In the final stage the behaviour is apparently governed by relaxation.

It should be noted that figure 5.7 is equivalent to a plot of the diffusion coefficient versus the (average) concentration. Hence the conventional interpretation of pseudo-Fickian behaviour, namely that the diffusion coefficient decreases with the concentration, is valid and can form the starting point for an alternative model. This approach will not be considered here.
We conclude that the pseudo-Fickian behaviour of the water absorption in our coatings agrees best with the relaxation model of Berens and Hopfenberg. In the next paragraph we show that this phenomenological model can be given a physical basis in terms of relaxation of the free volume in the coating.

5.11 Free-volume relaxation model
The Berens-Hopfenberg model, eq. 5.49, differs fundamentally from other relaxation models, in the sense that relaxation is here considered a mechanism that effectively increases the overall sorption. This means that the rearrangement of the polymer chains in response to the penetrant tends to increase the available free volume. This aspect was already stressed in the original paper of Berens and Hopfenberg\(^{26}\): "The relaxation processes appear to be related to slow redistribution of available free volume through relatively large scale segmental motions in the relaxing polymer." Rogers\(^{29}\) has formulated the same idea rather differently: "The penetrant molecules tend to loosen the polymer structure locally and make it easier for subsequent molecules to enter in the neighbourhood of the first than to go elsewhere."

On the basis of the above ideas a more fundamental free-volume relaxation model can be constructed. First we define \(\alpha(\tilde{r},t)\) as the available free volume per unit volume. We now reformulate the basic assumptions of Berens and Hopfenberg and Rogers as follows. Due to polymer relaxation \(\alpha\) tends towards a quasi-equilibrium state, characterised by an available free volume \(\bar{\alpha}\) that
increases as a function of the local concentration $c(\mathbf{r},t)$. This means that the time
dependence of the available free volume is given by the relaxation equation

$$\frac{\partial \alpha}{\partial t} = \frac{1}{\tau_r}(\alpha - \bar{\alpha}(c)) \quad (5.54)$$

Since the penetrant is only located in the available free volume, it is convenient to
introduce $\bar{c}(\mathbf{r},t)$, the concentration in the available free volume.

$$\bar{c} = c / \alpha \quad (5.55)$$

Diffusion tends to distribute the penetrant homogeneously over the available free
volume. The diffusional flux is therefore proportional to the gradient of $\bar{c}$. For the
one-dimensional case one has

$$j_z = -D \frac{\partial \bar{c}}{\partial z} \quad (5.56)$$

This flux can be substituted in the usual continuity equation

$$\frac{\partial c}{\partial t} = -\frac{\partial j_z}{\partial z} \quad (5.57)$$

For a coating of thickness $L$ the following boundary conditions for the
concentration are appropriate, cf eq.5.16

$$\bar{c}(z,0) = 0 \quad \bar{c}(0,t) = \bar{c}_\infty \quad \frac{\partial \bar{c}(L,t)}{\partial z} = 0 \quad (5.58)$$

For the available free volume $\alpha$ we choose units such that for the dry coating the
value is equal to unity. This must also be the initial value of $\bar{\alpha}$.

$$\alpha(z,0) = \bar{\alpha}(z,0)=1 \quad (5.59)$$

The quasi-equilibrium state at saturation will be denoted by $\alpha_{\infty}$, with $\alpha_{\infty} \geq 1$. Note
that this is then also the saturation value of $\alpha$. To complete the model the
concentration dependence of $\bar{\alpha}$ has to be specified. For simplicity we assume
that it increases linearly with the concentration $c$. 

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\[ \bar{\alpha}(c) = 1 + (\alpha_\infty - 1) \frac{c}{\alpha_\infty \bar{c}_\infty} \]  

(5.60)

Using eqs. 5.54 to 5.60 the accessible volume fields \( \alpha \) and \( \bar{\alpha} \) and the concentration fields \( c \) and \( \bar{c} \) can be calculated as a function of position and time. Finally the saturation function can be found from

\[ \psi(t) = \frac{1}{L} \int_0^L c(z,t)dz \]  

(5.61)

To show that this model is an extension of the Berens-Hopfenberg model, we consider the limiting case \( \tau_R >> \tau_D \equiv L^2 / D \). Then the differential equations decouple. At short times diffusion rules, undisturbed by relaxation. At long times relaxation takes over, with an instantaneous diffusion contribution. So one finds

\[ \psi(t) = \frac{1}{\alpha_\infty} \psi_0(t/\tau_D) + \frac{(\alpha_\infty - 1)}{\alpha_\infty} \left(1 - \exp(-t/\tau_R)\right) \]  

(5.62)

Thus the Berens-Hopfenberg result, eq. 5.49, is obtained, with \( A_D = 1/\alpha_\infty \). In the previous paragraph it was demonstrated that for this limiting case \( (\tau_R >> \tau_D) \) pseudo-Fickian behaviour is found. To solve the model for the general case numerical methods must be used. Preliminary calculations using a finite difference method indicate that for \( \tau_R > \tau_D \) the model quite generally yields pseudo-Fickian behaviour, similar to the Berens-Hopfenberg model.

We conclude that relaxation of the free volume of the coating, due to polymer rearrangement and water clustering, can satisfactorily account for pseudo-Fickian behaviour of water permeation in glassy polymers.

### 5.12 Conclusions

In section 5.4 it is shown that the capacitance curve as a function of time is dominated by the diffusion process. The choice of the effective medium theory is of minor importance. Analysis of the \( C(t) \) shows that the water permeation in our coatings deviates from ideal-Fickian diffusion. This points out in the direction of pseudo-Fickian diffusion. Water diffusion can not be described with a single time
constant \( \tau \). Therefore the asymptotic methods based on ideal-Fickian diffusion are useless. Opposite to literature in which for most polymers an increasing diffusion rate has been reported, a decreasing diffusion rate is found for our coatings. This is clearly demonstrated in the \( x(t) \) and \( \tau(t) \) plots. The transformation \( C(t) \rightarrow \psi(t) \rightarrow x(t) \rightarrow 1/\tau(t) \) is a tool to analyse deviation from ideal-Fickian diffusion and enable one to construct an improved model for diffusion. The permeation process can approximately be described by two time constants, \( \tau_s \) for long times and \( \tau_o \) for short times. It is shown that \( \tau_s \) is larger than \( \tau_o \). In section 5.10 it is concluded that although both relaxation processes and statistical effects from pore geometry can explain the pseudo-Fickian diffusion, relaxation processes are most probable. Diffusion influenced by free-volume relaxation is responsible for the sorption behaviour at long exposure times. In section 5.11 it is shown that phenomenological model of Berens-Hopfenberg can be given a physical basis. It is also proved that the diffusion and relaxation can be considered as independent processes. In figure 5.8 it is schematically summarised.

**Figure 5.8 Interpretation of pseudo-Fickian diffusion**
Acknowledgements
The author want to express their gratitude to prof. dr. ir. J. van Turnhout for his suggestions and critical remarks and to dr. ir. E.P.M. van Westing for the data sets of some water permeation measurements. The author wish to thank in particular dr. M.M. Wind for his assistance with the interpretation of the measurements.

Appendix 1
Eq. 5.13 yields an expression for the saturation function, independent on the geometry of the water distribution in a coating. To simply account for the water distribution in a coating the coating is considered as a two layer model consisting of a dry bottom layer of thickness $L(1-\psi(t))$ (layer 2) and a wet top layer of thickness $L\psi(t)$ (layer 1). This is illustrated in figure 5.9.

![Diagram of a two layer model](image)

*Figure 5.9 Schematic representation of a two layer model*

Applying eq. 5.8 to the two layer model, the following relation holds

$$\frac{1}{\phi_s} \frac{1}{\varepsilon(t)} = \frac{\psi(t)}{\epsilon_{wet}} + \frac{1-\psi(t)}{\epsilon_{dry}}$$  \hspace{1cm} (A1.1)

where $\epsilon_{dry}$ is the dielectric constant of the dry layer 2 and $\epsilon_{wet}$ that of the saturated top layer 1. The saturation function $\psi(t)$ is zero at $t=0$, which gives the following expression for $\varepsilon(0)$:
\[ \frac{1}{\phi_s} \left( \frac{1}{\varepsilon(t)} - \frac{1}{\varepsilon(o)} \right) = \psi(t) \left( \frac{1}{\varepsilon_{\text{wet}}} + \frac{1}{\varepsilon_{\text{dry}}} \right) \]  \hspace{1cm} (A1.3)

At saturation of the coating \( \psi(t) \) is equal to one, yielding for eq. A1.3

\[ \frac{1}{\phi_s} \left( \frac{1}{\varepsilon(\infty)} - \frac{1}{\varepsilon(o)} \right) = \left( \frac{1}{\varepsilon_{\text{wet}}} + \frac{1}{\varepsilon_{\text{dry}}} \right) \]  \hspace{1cm} (A1.4)

The ratio of eqs. A1.3 and A1.4 gives

\[ \frac{1/C(\phi(t)) - 1/C_0}{1/C_s - 1/C_0} = \psi(t) \]  \hspace{1cm} (5.14)

It should be noted that the saturation function does not depend on the choice of the effective medium theories for the two layers.

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V FILIFORM CORROSION

"A STUDY OF MECHANISMS"
Chapter 6

FILIFORM CORROSION STUDIES

6.1 Introduction
The initiation and propagation of filiform corrosion as deduced from literature have been discussed in chapter 3. In this chapter the results of new detailed investigations on initiation and propagation are discussed. After a short summary of the experimental conditions in section 6.2, the results of studies on the initiation of filiform corrosion are described in section 6.3. In particular, the influence of pretreatments is discussed. In chapter 3, it was concluded that additional investigations are also required to support the assumed anodic undermining propagation mechanism for coated aluminium substrates. In section 6.4 the following factors are discussed in relation with anodic undermining:

- the oxygen supply through the tail of a filament,
- the corrosion properties of the aluminium substrate and the filament growth rate.

6.2 Experimental
Various types of coatings, a number of aluminium alloys and different pretreatments have been examined. Table 6.1 shows the sample specifications. The pretreatments of the Al 3103 alloy is given in detail in table 6.2. In case of the Al 3103 alloy two batches, denoted as samples "A" and "B", were studied. These batches have different corrosion properties which are caused by small differences in the production process. The composition of the Al 3103 alloy is given in table 6.3. For easy inspection, the coatings did not contain any pigments with exception of the glossy white pigmented polyester coating on Al 3103. Panels sized 10 x 15 cm.

The initiation of filiform corrosion was stimulated by exposure to hydrochloric acid vapour (37% HCl, Baker Analyzed) for 15 to 30 minutes. Then the samples were rinsed with distilled water and subsequently placed in the test chamber. Each substrate-pretreatment-coating combination was exposed in duplicate.
The samples were placed in a sample holder at an angle of about 20° to the vertical. The sample holder with the samples was put in a 15 litre test chamber of glass, placed in a thermostatic bath. On the bottom of the test chamber a saturated solution of sodium chloride was present, providing a fixed relative humidity related to the adjusted temperature. The test chamber was closed with a glass cover to maintain constant temperature and humidity. The temperature and relative humidity were measured with a built-in laboratory thermometer and hygrometer. The test temperature was fixed at 38 ± 2 °C and the relative humidity was 82 ± 2 %.

<table>
<thead>
<tr>
<th>Aluminium alloy</th>
<th>pretreatment</th>
<th>coating type</th>
<th>coating thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 2024 T3</td>
<td>clad layer</td>
<td>polyurethane (1)</td>
<td>22 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>epoxy-amine (1)</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>Al 5050</td>
<td>chromatised (anorcoat-R) grounded (grit P1200)</td>
<td>Epoxy (2)</td>
<td>range: 10 - 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkyd (3)</td>
<td>10 - 150</td>
</tr>
<tr>
<td>Al 3003</td>
<td>chromatised (anorcoat-R) grounded (grit P1200)</td>
<td>Epoxy (2)</td>
<td>range: 10 - 200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkyd (3)</td>
<td>10 - 150</td>
</tr>
<tr>
<td>Al 3103</td>
<td>• as delivered (no pretreatment) • acid degreased • alkaline degreased • sulphuric acid anodised • both sulphuric acid anodised and sealed • conventionally Cr(VI) chromatised • Anorcoat-R (4) • phosphatised • bömitised</td>
<td>polyester (4)</td>
<td>21 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkyd (3)</td>
<td>range: 10 - 150</td>
</tr>
</tbody>
</table>

Table 6.1 Sample specifications. (1) Supplied by Akzo-Nobel Coatings. (2) Epikote 862 (Shell) cured with Eurodur 43 (Schering). (3) Supplied by T.N.O. coatings. (4) Supplied by Hunter Douglas Europe.
Table 6.2 Specification of the pretreatments of Al 3103
<table>
<thead>
<tr>
<th>Si</th>
<th>Mn</th>
<th>Be</th>
<th>Fe</th>
<th>Mg</th>
<th>Pb</th>
<th>Cu</th>
<th>Sn</th>
<th>Ca</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>1.03</td>
<td>1 10^{-4}</td>
<td>0.58</td>
<td>0.24</td>
<td>4 10^{-3}</td>
<td>1 10^{-3}</td>
<td>2 10^{-3}</td>
<td>7 10^{-4}</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Table 6.3  Composition of alloy Al 3103 (wt.%). The elements Ti, Li and Cr could not be detected.*

After exposure during 1, 5 and 9 weeks the samples were inspected. A selection of the panels were photographed using a Neophot 30 light microscope. The length of the filaments was measured. The growth rate was calculated for most panels from the measured length after 1 and 9 weeks exposure. In some cases, e.g. the 3103 alloy, the growth rate was calculated only from the length after 9 week exposure. Small filaments (length smaller than 3 mm) were ignored for the calculation.

Scanning Electron Microscopy (SEM) pictures were made using a Jeol 840A scanning microscope. The accelerating voltage was 10 kV. A thin gold layer was deposited.

### 6.3 Initiation studies

The initiation of filiform corrosion is the formation of blisters, as has been discussed in chapter 6 in more detail. Blister formation and growth inevitably occur after a certain time when water, oxygen and salts are present at a coating defect. In our experiments some growth of blisters was always observed leading to initiation of filiform corrosion. This is obvious in figure 6.1. Initially a blister starts growing which after a certain time turns into uni-directional growth (a filament). For more detailed investigation of the head of the filament, the coating was mechanically stripped off after the sample had been dried for several weeks at elevated temperatures. Thus the electrolyte solution in the head of a filament, was evaporated and dry corrosion products remained. The corrosion products show circular structures (fig. 6.2), indicating circular growth of corrosion spots in the filiform head.

For effective inhibition of filiform corrosion in practical situations, the initiation of filiform corrosion, i.e. blister formation and growth (underfilm corrosion), should be retarded. Contamination at the coating-substrate interface with salts should be prevented. When the metal is contaminated before the application of the coating, for example by uncareful handling, salts present under the (intact) coating do
Figure 6.1  Blister formation near a line defect in an alkyd coating on Al 5050 alloy, bright field microscopy.

Figure 6.2  SEM pictures of the head of the filiform. Coating was stripped off mechanically after drying for several weeks at evaluated temperatures.
inevitably lead to osmotic blistering, eventually leading to filiform corrosion when exposed to the atmosphere. Also salt contamination of mechanical coating defects yields well conducting electrolyte solutions which in combination with oxygen facilitate corrosion processes. A reduction of the susceptibility to such corrosion phenomena is obviously obtained by regularly cleaning the coated surface of a construction.

There are reasons to believe that the initiation of blisters and the general corrosion properties of the aluminium alloy are closely related. At a coating defect the metal substrate is directly exposed to the atmosphere. As discussed in chapter 1 the metal surface starts immediately corroding at the defect where usually water and oxygen are present. The initiation of corrosion on (uncoated) aluminium alloys may start at local irregularities of the thin naturally present oxide layer on aluminium. These irregularities are caused by the precipitation of second phases (intermetallic phases) in the alloy. These local differences in composition influence the quality of the oxide layer over these phases, and as a consequence the protective properties. In particular when copper rich phases are present, the cathodic reaction preferably occur at these particles which may lead to local corrosion phenomena. It is therefore expected that the general corrosion properties of aluminium alloys are directly related to the initiation of blisters and filiform corrosion of the coated alloy. This is confirmed by an evaluation of filiform corrosion damage of many different construction parts, recently performed in Belgium\(^1\). The results showed that the composition of the alloy was important for the occurrence of filiform corrosion. Elements as copper and magnesium may precipitate as intermetallic phases at which filiform corrosion may initiate.

To retard local corrosion processes initiated at intermetallic phases in the alloy, a conversion layer can provide additional corrosion protection. The naturally present thin oxide layer is then replaced by a thick conversion layer which completely covers intermetallic phases. The effect of different pretreatments on the initiation for filiform corrosion was therefore examined. Especially the number of filaments was determined because the number is closely related to the susceptibility to initiation of filiform corrosion. Figure 6.3 shows the number of filaments for different pretreatments as acid and alkaline degreasing, anodising, phosphatising, bômitising and chromatising. Two batches of Al 3103, "A" and "B" were examined. Because of the different corrosion properties of the batches it was expected that the initiation susceptibility was different for these batches. The number of initiation
sites for batch "A" was found to be consistently smaller than that for "B" in case of the acid and alkaline degreased (no. 1 and 2) and the no pretreated sample (no. 0) (see figure 6.3).

![Diagram showing number of filaments versus the pretreatment of Al 3103. Polyester coating. 0 is no pretreatment, 1 acid degreased, 2 alkaline degreased, 3 sulphuric acid anodised, 4 sulphuric acid anodised and sealed, 5 conventionally Cr(VI) chromatised, 6 Anorcoat-R pretreatment, 7 phosphatised, 8 bömitised.]

However the influence of the pretreatment is enormous. Figure 6.3 shows that the number of filaments for the acid and alkaline degreased panels is considerably larger than for the other pretreatments. Initiation of the panels with pretreatment layers is apparently more difficult. This is due to the suggested barrier inhibition mechanism of the relatively thick conversion layer.

Especially for the "B"-panels, the number of filaments on the conventionally chromatised and Anorcoated panels is consistently smaller than that on the other pretreated panels (fig. 6.3). Initiation is well prevented due to the presence of electrochemically active corrosion Cr(VI) in the conversion layer. Although the number of filaments of both the anodised-sealed and the bömitised panels is not so small as for the chromatised panels (panel "B"), they are also not very susceptible for filiform corrosion of the coated substrate. Phosphatised samples behave worse.
6.4 Propagation studies
6.4.1 Oxygen transport in a filament

The propagation mechanism of filiform corrosion for coated aluminium substrates has been discussed in chapter 3. There is only a limited amount of experimental evidence in literature for the anodic undermining mechanism on coated aluminium substrates. pH measurements in the edge of a filament would provide evidence for this mechanism. In chapter 3 it was shown that these measurements are difficult since the anodic edge of a filament is quite narrow. However, studies with pH-indicators in primer coatings on coated aluminium alloys showed that the edge of a filament is indeed acid. This would confirm the anodic undermining mechanism. Results of other experiments are not so obvious. It was found that the growth rate of a filament is slightly retarded when its length increases (fig. 3.7). This result may indicate that the oxygen transport may take place through the tail as assumed in the anodic undermining mechanism. Another indication for this transport path was given in figure 3.8 where the growth rate of a filament on coated aluminium substrates was shown to be independent on the coating type for 14 different types of coatings. More experimental results are required to finally establish the anodic undermining mechanism for filiform corrosion on coated aluminium substrates.

Measurements were performed to investigate the oxygen transport path for coated aluminium alloys. Two types of experiments have been carried out. First, several layers of aluminium foil have been glued onto the coating surface at a distance of about 4 mm from the coating defect where filiform corrosion initiated. Initially the oxygen transport through the coating is not influenced in the filament growth zone. After longer exposure times when the filament reaches the part of the coating which has been covered by aluminium foil, the oxygen transport through the coating is completely blocked by these layers. The filament may then either grow further under the aluminium foil, or change its direction and continue its growth merely under the uncovered part of the organic coating. When the oxygen supply takes place through the tail, no effect of the aluminium foil on both the growth rate and the growth direction of the filaments is expected. However, when the filaments would change their direction and continue their growth only under the uncovered organic coating, obviously oxygen is supplied through the coating. This would also imply that the propagation mechanism is cathodic delamination as has been described in section 3.3.1. For cathodic delamination the growth rate depends considerably on the permeation properties of the coating.
as has clearly been demonstrated for the filament and blister growth rate on coated steel substrates. A significant effect of the coating type on the growth rate is expected in that case.

Secondly, in another type of experiment, the coating defect, where a filament had initiated, was sealed by an epoxy coating. The tail and the head of the filiform were left unattended. These experiments have only been performed to check the mechanism derived from the first type of experiments. For anodic undermining, the propagation of a filament should stop when the coating defect is completely sealed.

The results of these experiments are now discussed. The measurements show that the aluminium foil layer on the organic coating does not affect the direction and the growth rate of the filaments. The latter result is derived from the fact that the mean length of the filaments on these panels is equal to that on the reference panels without aluminium foil layers on the organic coating. These results were found for all types of coating binders after 5 weeks of exposure. The corrosion rate of a filament was calculated from the depth of corrosion into the metal, the width and the growth rate. Table 6.4 shows the results of this calculation for various coating thicknesses and for different coating types. Some results from literature are also shown.

<table>
<thead>
<tr>
<th>Coating</th>
<th>thickness (μm)</th>
<th>Substrate</th>
<th>corrosion rate $10^{-6}$ cm$^3$ day$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyurethane 1,2</td>
<td>±30</td>
<td>Al 7075 T6 or Al 2024 T3 clad</td>
<td>6.7</td>
</tr>
<tr>
<td>21 different 4</td>
<td>26 - 35</td>
<td>Al 3003 H14 Q-panel</td>
<td>6.0 ± 2.0</td>
</tr>
<tr>
<td>polyurethane (a)</td>
<td>22 ± 2</td>
<td>Al 2024 T3 clad</td>
<td>5.4 ± 2.0</td>
</tr>
<tr>
<td>epoxy-amine (a)</td>
<td>22 ± 2</td>
<td>Al 2024 T3 clad</td>
<td>8.0 ± 2.0</td>
</tr>
<tr>
<td>alkyd (a)</td>
<td>10 - 150</td>
<td>Al 3003, grounded</td>
<td>3.8 ± 2.0</td>
</tr>
<tr>
<td>alkyd (a)</td>
<td>10 - 150</td>
<td>Al 5050, grounded</td>
<td>2.1 ± 1.2</td>
</tr>
<tr>
<td>polyester (a)</td>
<td>21 ± 2</td>
<td>Al 3103, acid degreased</td>
<td>12 ± 3.5</td>
</tr>
</tbody>
</table>

Table 6.4 The filament corrosion rate determined from photographs for various coating thicknesses and types of binder after 5 weeks of exposure.

(a) our results. Holler\textsuperscript{4} exposed the panels to 85% R.H. and 23°C while our experiments are performed at 82±2% R.H. and 38±2°C. Hoch\textsuperscript{1,2} exposed the panels to 75% R.H. and room temperature.
Table 6.4 shows that the rate is virtually independent on coating thickness and type of coating. From this it is concluded that the oxygen is supplied through the filament and as a consequence the anodic undermining mechanism determines the propagation rate of filiform corrosion. The second type of experiments confirms this conclusion. When the coating defect was sealed, the growth rate was remarkably slowed down. The filiform growth did not stop completely, probably due to the fact that the epoxy coating used for the seal, is still a little bit permeable for oxygen.

6.4.2 Influence of pretreatments

It was demonstrated in the previous section that for coated aluminium substrates the propagation mechanism is anodic undermining. Since the oxygen supply through the tail of a filament is generally assumed to be quite fast\(^5\), the oxygen transport does not inhibit the cathodic reaction, i.e. the oxygen reduction reaction. As a consequence the rate of the anodic reaction, occurring in the edge of a filament, may control the propagation rate of a filament. The anodic reaction rate generally depends on the corrosion properties of the aluminium alloy. So it is expected that the growth rate of a filament is related to the corrosion properties of the aluminium alloy.

The corrosion properties of aluminium can be improved by a pretreatment layer. Well-known are anodised, phosphatised and chromatised layers. Another positive effect of such layers is that they also improve the adhesion strength of the coating. In chapter 3 it was discussed that the adhesion strength is closely related to the propagation rate of filiform corrosion. Different pretreatments were examined for the Al 3103 alloy. These were shown in table 6.2. It should again be noted that two bathes of the Al 3103 alloy are examined on their filiform corrosion susceptibility, noted as "A" and "B", with different corrosion properties as observed in industrial practice.

After 9 weeks exposure it was found that the lengths of the filaments were quite different for the differently pretreated panels. The length varied between 5 mm for the anodised samples to about 150 mm for the acid and alkaline degreased samples. The polarisation curves in chapter 5 showed that also the passive current density varied significantly for the differently pretreated samples. The passive current density reflected the corrosion rate of the aluminium substrate in the passive state. Therefore the corrosion rate of our samples was ranged on basis of their passive current density (fig. 6.4). The smallest corrosion rates were
Figure 6.4  The relative current density for the Al 3103 alloy with different conversion layers, batch "A". All panels are ranked to sample no 4 (=1). The measured passive current density of this sample was 3.32 nA/cm².

0 is no pretreatment, 1 acid degreased, 2 alkaline degreased, 3 sulphuric acid anodised, 4 sulphuric acid anodised and sealed, 5 conventionally Cr(VI) chromatised, 6 Anorcoat-R pretreatment, 7 phosphatised, 8 bōmitised.

observed for the anodised and anodised plus sealed samples. The other pretreatments can now be ranked. The first group of samples which had similar high corrosion rates, were the not pretreated (as delivered), acid or alkaline degreased, and the phosphatised samples. The naturally present oxide layer or the phosphate conversion layer is not able to provide an effective barrier layer for corrosion protection. The samples which were conventionally chromatised, Anorcoated or bōmitised had similar medium corrosion rates.

When the rate of the anodic reaction controls the overall propagation rate of a filament, the passive current density can be considered as a measure for the propagation rate. Consequently, the current density at slightly anodic potentials, was compared with the mean length of the filaments after the filiform corrosion tests. In figure 6.5 the current density at 500 mV (vs. OCP) is plotted versus the length of the filaments for batch "A", coated with a polyester coating. This is a typical plot which is also found for the alkyd coatings and for batch "B". It should be noted that the curve is independent on the exact choice of the anodic potential.
Figure 6.5 The current density at 500 mV vs. OCP versus the length of the filaments for Al 3103, batch "A". The samples were differently pretreated, and coated with a polyester coating.

0 is no pretreatment, 1 acid degreased, 2 alkaline degreased, 3 sulphuric acid anodised, 4 sulphuric acid anodised and sealed, 5 conventionally Cr(VI) chromatised, 6 Anorcoat-R pretreatment, 7 phosphatised, 8 bûmitised.

From the linear relation in figure 6.5 it is concluded that the filament growth rate is determined by all processes influencing the passive current density which includes both the transport phenomena of ionic species like aluminium and oxygen ions across the conversion layer and the reactions occurring at the interfaces (metal-conversion layer and conversion layer-coating interface). In other words the propagation rate of a filament depends on the quality of the conversion or oxide layer.

Results from literature can be understood on basis of the found relation between corrosion properties of the substrate and the propagation rate of filiform corrosion, determined by anodic undermining.

It has been reported that the resistance against filiform corrosion is much better when the weight gain of Cr(VI) of the chromatised pretreatment increases from 200 mg/m² to 600 mg/m², i.e. with increasing thickness of the conversion layer. Scheck also examined the effect of the thickness of anodised layers on the filament growth rate. He also found that the growth rate is considerably retarded.
with the thickness of the anodised layer. In fact, he found a linear decrease of the area of a filament with the inverse of the layer thickness (fig. 6.6). This curve is hardly influenced by the coating type. On the other hand, it was also found in literature that the passive current density decreases with increasing thickness of the oxide layer. For a small thickness increase, an inverse relation between thickness and passive current has been reported confirming the suggested relation between the general corrosion properties of the substrate-conversion layer system and the propagation rate (length) of the filaments.

No significant difference between the growth rates of the filaments on samples "A" and "B" was observed. The influence of the pretreatment method on the corrosion rate is apparently much larger than small differences due to chemical composition and production method.

In section 6.2 where initiation has been discussed, it was shown that the initiation of filiform corrosion for the anodised panels is much easier than for the chromatised panels. According to chapter 1, this is due to the fact that anodised samples obtained their corrosion protection only by the barrier layer mechanism whereas for chromatised alloys the active inhibition mechanism also plays a role. Active components like Cr(VI) in the chromate conversion layer will repair damaged sites in the oxide layer, resulting in a smaller number of initiation sites.
Active species in conversion layers are thus most effective for the inhibition of the initiation of filiform corrosion. The propagation rate could in principle also be lowered by these species but in practice no significant retardation was found for our samples. When the coating was stripped off from the filament it became clear that the conversion layers had been considerably attacked. The layers dissolve chemically due to the low pH in the head of the filament. Although electrochemically active species in chromate conversion layers in principle repair the attacked sites of the oxide layer, the concentration of these species is finite. Therefore they act for a limited period of time.

In literature it has often been mentioned that the (chemical) adhesion strength may increase when aluminium is pretreated\(^9\). Different pretreatments result in differences of the chemical adhesion strength of a coating. It was found in section 3.4 that the propagation rate of filiform corrosion also considerably depends on the adhesion strength of the coating. Unfortunately no adhesion strength measurements have been performed for our differently pretreated samples. However, from the obviously found relation between the corrosion properties of the substrate (metal plus conversion layer) and the mean growth rate of a filament, it can be concluded that differences in chemical adhesion of the coating are apparently of minor importance. Figure 6.6 shows that the type of coating only slightly influences the area of a filament and thus confirms our conclusion.

6.5 Conclusions and recommendations for further research

The overall filiform corrosion performance of a coated alloy is determined by the susceptibility of a coated aluminium alloy for corrosion initiation and by the propagation rate of a filament. Both stages, initiation and propagation, depend on the corrosion behaviour of the substrate and can be improved by pretreating aluminium alloys before coatings are applied.

The initiation susceptibility is certainly reflected in the number of filaments present after a fixed time of exposure. The easier the initiation the more filaments are formed. The number of filaments for the samples which have only been acid or alkaline degreased is larger than that of the panels with pretreatment layers. The initiation on these panels is thus much easier which may be attributed to second phase precipitates. These phases may lead to local attack at weak spots in the oxide layer and as a consequence to different local corrosion rates. The initiation
of blistering and filiform corrosion can thus be inhibited when these phases are completely covered by an additional (conversion) layer. The protection is most effective when also electrochemically active species are present in the conversion layer. This is clearly demonstrated by the results of the chromatised panels. Cr(VI) in the conversion layer may immediately repair the passive layer when it is damaged. In order to prevent filiform corrosion damage in practice a large number of recommendations for the specifications of the aluminium alloys, production and conditions of storage of pre-finished constructions have been given\textsuperscript{10}. Most of these concern factors which influence the initiation stage of filiform corrosion like the creation of coating defects during service or handling, and the contamination of the coating defects with salts.

The mechanism for the transition from initiation (i.e. blistering and underfilm corrosion) to uni-directional growth remains unclear. Further research is necessary to elucidate the main factors which effects this transition.

The propagation mechanism on aluminium alloys is obviously anodic undermining. The oxygen transport takes place through the tail of a filament. This means that the oxygen permeability of coatings is of minor influence. Research in the field of oxygen permeation of organic coatings is thus not useful. For filiform corrosion at coated steel however the permeation properties of the coating are of major importance for the growth rate as has been discussed in chapter 3. It is thus expected that for coated steel substrates filiform corrosion can considerably be retarded by coatings with barrier pigments for oxygen diffusion.

It has been clearly demonstrated that the corrosion properties of aluminium substrates are related to the growth rate of a filament. A pretreatment layer improves the corrosion properties of an alloy and therefore it retards the filiform propagation rate. Coated aluminium alloys which have poor corrosion properties may obtain reasonable resistance against filiform corrosion when they are pretreated with conversion layers.

The smallest filament growth rate was observed at the anodised samples, the largest rates for the samples which were no pretreated, alkaline or acid degreased, or phosphatised. The naturally present oxide layers on the degreased panels and the phosphate conversion layer are not enable to provide an effective barrier layer that can reduce the corrosion rate. It is striking that the anodised samples yield very small propagation rates. The rate is even smaller than that of
the chromatised panels. From this and the fact that conversion layers chemically
dissolve in the filament head, it is believed that the presence of electrochemically
active species is of minor importance for the retardation of the propagation rate of
filiform corrosion. However, the number of filaments of the anodised panels
(initiation) is much larger and as a consequence the overall filiform corrosion
performance is rather similar.

No significant difference in growth rates has been observed between the two
different batches "A" and "B". The number of initiation sites differs slightly
between the batches "A" and "B", in particular for the no pretreated, acid and
alkaline degreased samples.

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VI  GENERAL CONCLUSIONS
Filiform corrosion starts with the formation of a blister at a coating defect. The initiation of corrosion in a coating defect depends on the corrosion properties of the substrate. Chromate conversion layers are very effective in corrosion inhibition. This is due to the electrochemically active Cr(VI) in the conversion coating which is reduced as the layer is damaged. The layer is then self-repairing (active inhibitive mechanism). As a result, the number of filaments initiated at a line defect is very small. When no electrochemically active species are present, as for anodised aluminium, the corrosion inhibition can only be provided by the barrier mechanism of the conversion layer. Corrosion may then initiate and propagate when the conversion layer is damaged. The number of initiation sites is found to be considerably larger than for the chromatised aluminium samples.

Subsequently the blisters turn into filaments. The transition of blister growth to uni-directional growth is still unclear. The propagation mechanism of filiform corrosion on coated aluminium substrates is anodic undermining. It was shown that the oxygen transport takes place through the tail of the filament and is found to be independent on the oxygen permeation properties of the coating. Since the oxygen supply through the tail is quite large, the propagation rate of the filament is determined by the rate of the anodic reaction in the head of the filament. Consequently, the corrosion properties of the aluminium alloy effect the propagation rate of a filament, which can be considerably reduced by pretreating aluminium alloys. The relation between the corrosion properties of the alloy and the filament growth rate was confirmed by the fact that a relation was found between the passive current and the propagation rate of a filament. So, the growth rate depends on the transport of aluminium and oxygen ions across the (conversion) layer and the interfacial reactions. Coated anodised aluminium shows a very small growth rate of the filaments, although their initiation is quite fast. On the other hand the propagation rate of chromatised aluminium is much larger than that of anodised aluminium. The initiation of these samples is difficult.

The passive film on aluminium was studied using impedance measurements. For the interpretation the Point Defect Model, proposed by D.D. Macdonald, was applied. This model was adjusted to describe the impedance data correctly since the inductive loop at intermediate frequencies can not described by Macdonalds original model. It was shown that adsorbed oxygen ions at the oxide-solution interface can account for the inductive loop, observed in our impedance data at intermediate frequencies.
The permeation properties of an organic coating can be studied using capacitance measurements. The coating capacitance increases as a result of the increase of the dielectric constant of the coating when water penetrates the coating. The shape of the curve of the coating capacitance as a function of exposure time is determined by the diffusion model. The effective medium theory, which relate the coating capacitance to the volume fraction of water in the coating, is of minor importance when the maximum amount of absorbed water (solubility) is small. All coatings have a small solubility (2 to 5 \(^\text{v}\%\)). A new method was developed to analyse the measurement data. Deviations from ideal-Fickian behaviour can be determined and incorporated into a new improved model for non-Fickian diffusion. To facilitate water penetration into the coating, relaxation of the polymer structure has to take place. Hence the diffusion mechanism of water changes, resulting in a pseudo-Fickian diffusion behaviour. This can be described by a free-volume relaxation model.
In this thesis the results are presented of a study to filiform corrosion. This study deals with the mechanism of filiform corrosion, the corrosion behaviour of aluminium alloys and the water permeation of organic coatings.

Corrosion of coated metal substrates initiates at coating defects. Two cases are often considered in literature.

The first case describes the situation where adhesion fails at the coating-substrate interface, e.g. due to the presence of a salt particle, while the coating is still intact. A blister may then be formed due to osmosis. The growth rate of a blister depends on the adhesion properties of the coating.

The second case occurs when the coating fails due to the pressure of the formed corrosion products or when the coating is damaged mechanically. The metal substrate is then exposed directly to the aggressive environment. Corrosion may start at weak spots in the passive film, e.g. at precipitates of intermetallic phases.

The propagation mechanisms of coated substrates under immersion are anodic undermining and cathodic delamination. A different path length for oxygen diffusion to the coating-substrate interface at different sites results in the formation of a differential aeration cell. The anodic and cathodic reactions are then spatially separated in the blister. For anodic undermining the anodic reaction takes place in the edge of the blister whereas for cathodic delamination the cathodic reaction (oxygen reduction) does. Anodic undermining occurs in case of coated aluminium alloys and cathodic delamination in case of coated steel substrates. This is caused by the fact that Fe(II) is oxidised to Fe(III), reducing the oxygen that diffuses across the corrosion products. Therefore the oxygen supply through the defect and corrosion products is limited and overruled by the oxygen supply through the coating in the edge of the blister.

Filiform corrosion starts with the formation of and growth blisters. The factors, influencing the initiation of blisters, are also important for the initiation of filiform corrosion phenomena. The blisters may subsequently grow into uni-directional filaments. The factors which govern this, are unknown.
Similar to corrosion of coated substrates under immersion, the propagation mechanisms of filiform corrosion are anodic undermining (coated aluminium alloys) and cathodic delamination (coated steel substrates). The oxygen supply to the active head takes place through the tail of the filament in case of anodic undermining. This diffusion process is rather fast and as a consequence the propagation rate is determined by the rate of the anodic reaction in the head of the filament. The results of the measurements show clearly that the propagation rate depends on the corrosion properties of the alloy. Conversion layers improve considerably the corrosion properties of aluminium alloys and hence retard the filament growth rate. It has been shown that the rate of filiform corrosion is determined by all processes influencing the passive current density which includes both the transport phenomena of ionic species like aluminium and oxygen ions across the conversion layer and the reactions at the interfaces. Coated anodised aluminium showed a very small propagation rate, compared to coated chromatised aluminium. However the initiation is much faster for anodised aluminium. This is due to the fact that Cr(VI) is able to repair the oxide film when it is locally damaged.

For cathodic delamination, the oxygen is supplied through the coating. Thus the permeation properties of the coating for oxygen are quite important for the propagation rate.

Secondary factors influencing the growth rate of a filament are the adhesion properties of the coating and contamination of the coating-substrate interface with salts. In the latter case the conductivity of the electrolyte solution in the coating defect increases, which may stimulate the local corrosion process. There is in general sufficient water present in the coating since at exposure to a humid atmosphere the coating is saturated with water. Water transport to the filament head is provided by osmosis.

The corrosion behaviour of aluminium alloys is determined by the protective properties of the passive film. These properties can be studied using impedance measurements. The processes at the interfaces and in the passive film yield different time constants, which can be observed in the impedance data. In literature there is no consensus on the origin of the different time constants. The application of the point defect model, proposed by D.D. Macdonald, provides a physical model that is in principle able to account for most of the measured impedance data. The point defect model concerns only point defects and neglects any higher order lattice defects. At the interfaces electrochemical reactions occur.
which produce or consume vacancies. The aluminium ion or oxygen ion vacancies are transported across the passive film under influence of a high electric field. The impedance measurements of passive aluminium show in most electrolyte solutions an inductive loop at intermediate frequencies. This phenomenon can not be explained by Macdonald's point defect model. Hence the point defect model was adjusted. The inductive loop is attributed to adsorbed oxygen ions at the oxide-solution interface. It has been shown that the incorporation of adsorbed oxygen ions at the oxide-solution interface into the reaction mechanism of the point defect model can account for the inductive loop at intermediate frequencies.

The permeation and sorption of water in eight coatings below the glass-transition temperature has been monitored using capacitance measurements. For each coating deviations from ideal-Fickian diffusion were observed. The diffusion rate was found to decrease considerably with time of exposure. This anomalous or non-Fickian behaviour is known as pseudo-Fickian diffusion. To analyse the measurements further a new method is developed. The data are transformed to a time dependent diffusion rate. The analysis results in a new pseudo-Fickian diffusion model, which can also be represented in terms of a spectral distribution of diffusion rates. The results agree quite well with the relaxation model of Berens and Hopfenberg. The Berens-Hopfenberg model in particular, and pseudo-Fickian behaviour in general can be understood as diffusion influenced by free-volume relaxation.

The following general conclusions can be drawn from the experiments, described in this thesis:

- Both the initiation and propagation of filiform corrosion determine the performance of substrate-conversion layer-coating system. This was shown by experiments with the anodised and chromatised panels. The propagation mechanism of filiform corrosion in case of coated aluminium substrates is obviously anodic undermining. The corrosion properties of the metal-conversion layer system is important for the propagation rate of a filament.
- The impedance measurements can be interpreted using the point defect model of D.D. Macdonald, which was slightly adjusted to account for the inductive loop at intermediate frequencies. The inductive loop can be attributed to adsorbed oxygen ions at the oxide-solution interface.
• Finally a new method is developed to analyse the capacitance measurements, performed during the immersion of organic coatings in water. It was shown from the analysis of the water uptake experiments that both diffusion and relaxation of the polymer structure take place.
SAMENVATTING

FILIFORME CORROSIE BIJ GEVERFDE ALUMINIUM PANELEN
"DE BESTUVERING VAN HET MECHANISME"

In dit proefschrift worden de resultaten besproken van een studie naar de mechanismen van filiforme corrosie. Na een inleiding over de algemene corrosie mechanismen van geverfde metalen panelen, worden de mechanismen van filiforme corrosie besproken aan de hand van literatuurgegevens en nieuwe experimentele resultaten. Ook wordt ingegaan op het corrosiegedrag van (niet geverfd) aluminium en op de waterpermeatie van verflagen.

Corrosieverschijnselen van geverfde panelen beginnen bij defecten in de verlaag. Twee gevallen worden hierbij in de literatuur meestal onderscheiden.

In het eerste geval hecht de verlaag niet aan het metalen paneel, bijvoorbeeld tengevolge van een zoutkorreltje dat aanwezig was op het paneel voordat het geverfd werd. De continuïteit van de verlaag hoeft in dit geval niet verstoord te zijn. Osmotische processen resulteren dan in de vorming en groei van een blaar. De groeisnelheid hangt af van de hechtingseigenschappen van het substraat-verf systeem.

In het tweede geval is de verlaag beschadigd geraakt. Het metalen paneel staat dan in direct contact met de agressieve omgeving. Corrosieverschijnselen kunnen beginnen bij zwakke plaatsen in de oxyde laag op aluminium. Zulke zwakke plaatsen kunnen een gevolg zijn van de aanwezigheid van precipitataten in een legering.

De propagatiemechanismen van een blaar zijn anodische ondermijning en kathodische delaminatie. Deze mechanismen zijn gebaseerd op het principe van de differentiële beluchtingscel. Hierbij is de concentratie zuurstof op verschillende plaatsen op de verlaag-substraat grenslaag verschillend. Dit verschil kan bijvoorbeeld worden veroorzaakt door een verschil in de diffusielengte van zuurstof naar het metalen paneel. Een ruimtelijke scheiding tussen de plaatsen waar de anodische en kathodische reacties in een blaar plaatsvinden is het gevolg. In het geval van anodische ondermijning verloopt de anodische reactie in
de rand van de blaar en de kathodische reactie in het centrum. Bij kathodische delaminatie is dit omgedraaid, d.w.z. de kathodische reactie vindt plaats in de rand en de anodische reactie in het centrum van de blaar. Anodische ondermijning treedt op bij geverfde aluminium panelen terwijl kathodische delaminatie optreedt in geval van geverfde stalen panelen.

Filiforme corrosie begint met de vorming en groei van blaren zoals hiervoor is beschreven. De factoren die hierbij een rol spelen, zijn ook bepalend voor de initiatie van filiforme corrosie. Na de vorming en groei van blaren groeit de filiform uit in één richting. De grootheden die deze overgang bepalen, zijn niet duidelijk. De propagatiemechanismen van filiforme corrosie zijn evenals bij de groei van blaren, anodische ondermijning (in geval van geverfde aluminium legeringen) en kathodische delaminatie (in geval van stalen panelen). De aanvoer van zuurstof naar de kop van de filiform vindt bij anodische ondermijning plaats via de staart van de filiform. Bedekking van de verflaag met een niet permeabele aluminium laag beïnvloedde de richting van de filiformgroei als de propagatiesnelheid. Het diffusieproces van zuurstof door de staart is relatief snel. Hierdoor wordt de propagatiesnelheid van filiforme corrosie bepaald door de snelheid van de anodische reactie in de kop van de filiform. De propagatiesnelheid hangt dus af van de corrosie-eigenschappen van de aluminium legering die sterk beïnvloed kunnen worden door de aanwezigheid van conversielagen. Teneinde de gesuggereerde relatie tussen corrosie-eigenschappen en de propagatiesnelheid van filiforme corrosie nader te onderzoeken, werd een Al 3103 legering verschillend voorbehandeld (o.a. anodiseren, sealen, chromateren, fosfateren en bömiteren). Uit corrosie- en filiformproeven bleek dat de propagatiesnelheid van een filiform afhangt van de (transport-) eigenschappen van de conversielag en de (corrosie) reacties aan de grensvlakken. Er bleek bovendien dat de initiatie van een filiform bij de gechromateerde panelen langzaam was tengevolge van de aanwezigheid van electrochemisch actieve Cr(VI) in de conversielag. De propagatiesnelheid was daarentegen relatief groot. Bij de geanodiseerde panelen werd een filiform relatief snel geïnitieerd maar de propagatiesnelheid was echter zeer klein.

De aanvoer van zuurstof in geval van kathodische delaminatie vindt plaats door de verflaag. De propagatiesnelheid van filiforme corrosie hangt dan af van de permeatie eigenschappen van de verflaag voor zuurstof. Secundaire factoren die de propagatiesnelheid beïnvloeden, zijn ondermeer de hechtingseigenschappen van het metaal-coating systeem en de aanwezigheid
van verontreinigingen op het metalen paneel (o.a. zouten) voordat het geverfd werd.

De corrosie-eigenschappen van aluminium legeringen worden voornamelijk bepaald door de eigenschappen van de aanwezige oxydehuid. Deze eigenschappen kunnen worden bestudeerd met behulp van impedantiemetingen. In de literatuur worden de resultaten van de impedantiemetingen aan aluminium in verschillende electrolyt oplossingen beschreven. De interpretatie van deze metingen is zeer moeilijk. Het is dan ook niet verwonderlijk dat er geen eenduidige verklaring bestaat voor de processen die een rol spelen bij het vertragen van corrosie door de oxydehuid op aluminium. Er is ook geen goed model voorhanden dat gebruikt kan worden bij de interpretatie. D.D. Macdonald heeft het puntfouten model voorgesteld dat in principe zeer geschikt is voor de interpretatie van de impedantiemetingen. In het puntfouten model spelen vacatures een grote rol bij de vorming en afbraak van de oxydelaag. Bij de reacties aan de grensvlakken (metaal-oxyde en oxyde-oplossing) worden aluminium-ion vacatures en zuurstof-ion vacatures gevormd. Deze vacatures lopen onder invloed van een electrisch veld door de laag en kunnen in principe beide bijdragen tot de groei van de oxydelaag. De meeste impedantiemetingen vertonen een zogenaamde inductieve lus. Dit verschijnsel kan niet worden beschreven met het originele puntfouten model van D.D. Macdonald. Het puntfouten model is in dit proefschrift aangepast teneinde de inductieve lus te kunnen verklaren. Deze lus kan toegeschreven worden aan geadsorbeerde zuurstof ionen op het grensvlak van het oxyde met de oplossing.

De water permeatie eigenschappen van acht verschillende verflagen zijn bestudeerd met behulp van capacititsmetingen. Alle verflagen zijn onderzocht in de glasachtige toestand. Het waterpermeatie gedrag wijkt af van het ideaal Fickse diffusiegedrag omdat de diffusie snelheid in de tijd aanzienlijk afneemt. Dit verschijnsel wordt pseudo-Fickse diffusie genoemd.

Een nieuwe methode om de wateropnamemetingen te analyseren wordt besproken. Hierbij worden de meetdata getransformeerd naar een tijdsafhankelijke diffusiesnelheid. Een nieuw pseudo-Ficks diffusie model wordt afgeleid uit de tijdsafhankelijke diffusiesnelheid. Mathematisch kan de afname van de diffusiesnelheid kan ook worden beschreven door een spectrale verdeling van diffusiesnelheden. De meetdata worden dan statistisch geinterpreteerd. Uit het analyseren van de tijdsafhankelijke diffusiesnelheid bleek dat er twee processen

De algemene conclusies van het onderzoek dat beschreven is in dit proefschrift zijn:
- De initiatie- en propagatie van een filiform bepalen beide de gevoeligheid van het metaal-conversielaag-verflaag systeem voor filiforme corrosie. Dit bleek uit de experimenten met geanodiseerde en gechromateerde panelen zoals hiervoor is beschreven. Het propagatie-mechanisme van filiforme corrosie in geval van geverfde aluminium panelen is anodische ondernijning. De corrosie-eigenschappen van het metaal-coversielaag systeem zijn hierbij van groot belang.
- Bij het mechanisme van de opbouw van de oxydelaag op aluminium spelen geadsorbeerde zuurstof ionen op het oxyde-electrolyt grensvlak een grote rol. Het mechanisme kan goed beschreven worden met het puntfouten model van D.D. Macdonald dat uitgebreid is met geadsorbeerde zuurstofionen op het oxyde-electrolyt grensvlak.
- Tenslotte is er een nieuwe methode geïntroduceerd om de capaciteitsmetingen tijdens de wateropname van verflagen te analyseren. Uit deze analyse is gebleken dat zowel diffusie als vrije volume relaxatie-processen een grote spelen.
CURRICULUM VITAE

DANKWOORD
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