Filmform Corrosion of Aluminium Alloys

The effect of microstructural variations in the substrate

Arjan Mol
Stellingen behorende bij het proefschrift

Filiform Corrosion of Aluminium Alloys
The effect of microstructural variations in the substrate

door Arjan Mol

1. In tegenstelling tot anodische deeltjes verhogen met name kathodische deeltjes in de matrix de filiform corrosiepropagatie op substraatoppervlakken. Verhoging van de concentratie kathodische deeltjes en verfijning van hun verdeling verhoogt de filiform corrosiegevoeligheid.
*Dit proefschrift (Hoofdstukken 2, 4 en 6).*

2. De filiform corrosiestroom, in dit proefschrift gedefinieerd als de stroom behorende bij het snijpunt van de kathodische tak van de polarisatiecurve in het katholyt en de anodische tak van de polarisatiecurve in het anolyt, correleert met de filiform corrosiepropagatie en totale aantasting van geëxposeerde aluminium legeringen, mits de kathodische stroom in het anolyt niet begrensd wordt. De grootte van de correlatiefactor hangt sterk af van het type legering(selementen).
*Dit proefschrift (Hoofdstukken 3 en 6).*

3. Applicatie van specifieke oppervlaktepatronen is een erg effectieve manier om begrenzing van de filiform corrosie-aantasting binnen het gebied van het oppervlaktepatroon te realiseren en optimalisatie hiervan biedt goede perspectieven voor toepassing in de praktijk.
*Dit proefschrift (Hoofdstuk 5).*

4. Het is onjuist om te stellen dat publicatie van Scanning Kelvin Probe resultaten beter achterwege kan blijven nu de “apparaat-technische ontwikkelingen van de Kelvin probe nog vooruitlopen op de theoretische inzichten”. Juist publicatie van resultaten en de interpretatie hiervan met correcte omkadering door mogelijkheden en beperkingen kan de kloof tussen theorie en experiment verkleinen: handelen zonder kennis is onvoorzichtig, maar kennis zonder handelen is laf.
*Stelling 1 bij: Spoelstra, Proefschrift, Technische Universiteit Delft, 1999.*
*Dit proefschrift (Hoofdstuk 4).*
5. Uit het onderzoek naar het effect van warmtebehandelingen op het extrusiegedrag van AA6063 moet geconcludeerd worden dat een gloeitijd van 24 uur op 250-450 ºC na standaard homogenisatie en afschrikken in water te kort is om een grofheid in microstructuren te verkrijgen die vergelijkbaar is met die welke waargenomen wordt onder industriële praktijkomstandigheden.  
_J. van de Langkruis, Proefschrift, Technische Universiteit Delft, 2000._

6. Daar het voor de overgrote meerderheid van onderzoekers menselijkerwijs onmogelijk is om op twee of meer terreinen deskundig te zijn, zouden zowel monodisciplinaire opleidingen als multidisciplinair onderzoek gestimuleerd moeten worden.  

7. Simplificatie van juridisch woordgebruik in de Nederlandse wetgeving en jurisprudentie zou bij de gewone burger voor meer begrip en maatschappelijk draagvlak zorgen.  
_Vrij naar: C. van Noortwijk, Proefschrift ‘Het Woordgebruik Meester’, Erasmus Universiteit Rotterdam, 1995._

8. Het onderscheiden van een mannen- en vrouwencompetentie voor sporten, waarbij fysieke vermogens van onderschikt belang zijn, zoals snookeren en darten, is slechts gebaseerd op historische ontwikkeling en zou vervangen moeten worden door een gemengde competitie.

9. Journalistiek is vaak niet meer dan een kladversie van de geschiedenis.

10. De kern van nationalisme en racisme is egoïsme.

11. Geen mens is volledig consistent in mening en daad.

Propositions
with the PhD Thesis

Filiform Corrosion of Aluminium Alloys
The effect of microstructural variations in the substrate

by Arjan Mol

1. Cathodic particles in the matrix stimulate the filiform corrosion propagation on substrate surfaces, in contrast to anodic particles which have little effect. The filiform corrosion susceptibility increases with the concentration and a finer distribution of the cathodic particles.

This thesis (Chapters 2, 4 and 6).

2. The filiform corrosion current, defined in this thesis as the current at the intersection of the cathodic part of the polarisation curve in the catholyte and the anodic part of the polarisation curve in the anolyte, correlates with the filiform corrosion propagation and total attack of exposed aluminium alloys, provided that the cathodic current in the anolyte is not limited. The value of the correlation factor strongly depends on the type of alloy(ing elements).

This thesis (Chapters 3 and 6).

3. Application of specific surface patterns is a very effective way of confining the filiform corrosion attack within the set boundaries of the surface pattern and optimisation offers good perspectives for application in practice.

This thesis (Chapter 5).

4. It is incorrect to propose that Scanning Kelvin Probe results ought not to be published while "the technical developments of the Kelvin probe are ahead of the theoretical insights". It is the publication of the results and the interpretation of these results, correctly surrounded by the possibilities and restrictions, that can reduce the gap between theory and experiment: action without knowledge is imprudent, but knowledge without action is faint-hearted.


This thesis (Chapter 4).
5. From the investigation of the effect of heat treatment on the extrusion behaviour of AA6063, it should be concluded that a heat treatment time of 24 hours at 250-450 °C after standard homogenisation and water quenching, is too short to obtain a coarseness in microstructures that can be compared to those observed under industrial conditions.

6. Since it is humanly impossible for the great majority of researchers to be an expert on two or more areas of research, both monodisciplinary education and multidisciplinary research should be encouraged.

7. Simplification of legal terms in Dutch legislation and jurisprudence would result in more understanding and public support.

8. The distinction between a male and female competence for sports, for which physical strength is of minor importance, such as snooker and darts, is only based on historical developments and should be substituted by a mixed competition.

9. Journalism often is nothing more than a draft of history.

10. The essence of nationalism and racism is egoism.

11. Not a single person is fully consistent in opinion and action.

12. Friendship should be added to the list of primary necessities of life: no-one can do without it.
Filiform corrosion of aluminium alloys
The effect of microstructural variations in the substrate

Filiform corrosie van aluminium legeringen
Het effect van microstructurele variaties in het substraat

Arjan Mol
Filiform corrosion of aluminium alloys
The effect of microstructural variations in the substrate

Filiform corrosie van aluminium legeringen
Het effect van microstructurele variaties in het substraat

Proefschrift

Ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir K.F. Wakker,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op vrijdag 1 december 2000 om 10.30 uur

door

Johannes Matheus Cornelis MOL

ingenieur luchtvaart en ruimtevaart
geboren te Breda
Dit proefschrift is goedgekeurd door de promotoren:
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Prof. dr. J.H.W. de Wit

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Technische Universiteit Delft
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The research described in this thesis was performed in the Groups ‘Microstructural Control in Metals’ and ‘Corrosion Technology and Electrochemistry’ of the Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL, Delft, The Netherlands. Part of the research was performed in close collaboration with the Aeronautical and Maritime Research Laboratory, Australian Defence Science and Technology Organisation and also with the Commonwealth Scientific and Industrial Research Organisation Australia.

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Introduction

In this chapter, an overview is given of the present insights into the influencing mechanism of the parameters that play an important role in the filiform corrosion process on aluminium alloys. Also the nature of localised corrosion phenomena on aluminium alloys is discussed extensively. It is shown that filiform corrosion is a complex phenomenon, involving contributions from the environmental conditions, the organic coating, the coating-substrate interface and the microstructure of the substrate (surface). Microstructural variations in the substrate influence the general and local electrochemical characteristics of the alloy and also the quality of the overlying oxide layer. For these reasons it can be argued that the microstructure of aluminium alloys plays an important role in the filiform corrosion susceptibility of aluminium alloys.

1.1 General introduction and background

Filiform corrosion, characterised by a thread-like corrosion trace, can be observed on coated aluminium, magnesium and steel substrates [1.1-1.3] when exposed to humid and aggressive conditions, such as present in maritime environments. It is usually observed underneath organic coatings, but occasionally is also observed under the naturally present
oxide layer or under a pretreatment layer only [1.1-1.5].
Filiform corrosion starts at defects in the coating such as cutting edges or local weak spots
in the coating. An example of filiform corrosion in practice in the automotive industry is
presented in Figure 1-1, showing filiform corrosion underneath a clearcoat on an
aluminium car wheel hub.

\[
\text{Figure 1-1: Practical example of filiform corrosion on a car wheel hub}
\]

This local attack is a complex phenomenon involving influences of the environmental
conditions, the organic coating, the coating-substrate interface and the substrate surface.

The local filamentary attack has been responsible for extensive damage, with extreme costs
in various sectors of industry, such as aircraft, building and automotive [1.6-1.10]. In
building industry it is a serious cosmetic problem for facades and window frames applied
in coastal areas. For aircraft, filiform corrosion may even result in more serious damage to
the structure when left unattended, depending on the application area of the alloy. Besides
the endangerment of the structural integrity of the aircraft structure, repairing the damage is
time consuming and costly. Repairing the attacked area either includes total replacement of
the attacked part or local stripping of the organic coating and removal of the corrosion
products (e.g. by glass bead blasting) and local application of a new conversion and organic
coating, which is cumbersome.
Filiform corrosion has gained interest of the aluminium, pretreatment and coating manufacturers and suppliers over the last decades due to the increased application of coated aluminium in the building and automotive industry. Many recent investigations [1.11-1.15] into the mechanism of filiform corrosion and the relevant parameters have resulted in a better understanding of the general and local filiform corrosion mechanism on aluminium. However, due to the many parameters involved, the influencing mechanisms of the relevant factors for filiform corrosion have not been established unambiguously. In the present investigation a systematic study was exerted to further elucidate the effects of microstructural variations in the aluminium substrate (surface).

1.2 Corrosion of aluminium alloys

1.2.1 Introduction

Corrosion can be defined as the electrochemical degradation of a metal. As indicated by its position in the electromotive series, aluminium is a reactive metal from a thermodynamic point of view: among structural metals only beryllium, magnesium and zinc are more reactive. Aluminium owes its excellent resistance to corrosion and its usage as one of the primary structural metals to the aluminium oxide film that is naturally formed on aluminium in the atmosphere and if damaged, reforms immediately in most environments [1.16]. On a surface freshly abraded and then exposed to air, this oxide film is only 5-10 nm thick but is highly effective in protecting the underlying aluminium surface from corrosion. The air-formed passive layer acts as an insulator and consists mainly of aluminium oxide which may be hydrated at the outer surface to form Al₂O₃·H₂O (AlOOH, boehmite) and Al₂O₃·3 H₂O (Al(OH)₃, gibbsite). The exact structure of the oxide film can be very complicated and depends on the environmental conditions during its formation [1.17].

The conditions for thermodynamic stability of the oxide film is expressed by the Pourbaix diagram [1.18]. This diagram indicates the passivity of aluminium (i.e. protection by its oxide film) in the pH range of about 4 to 8.5. This diagram shifts somewhat with temperature and the composition and structure of the oxide. Beyond the limits of its passive range, aluminium corrodes by simple electrochemical reactions, in both acidic and
alkaline environments, yielding $\text{Al}^{3+}$ ions in the former and $\text{AlO}_2^-$ ions in the latter, according to Equations 1-1 and 1-2 respectively:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- \quad \text{(1-1)}$$

$$\text{Al} + 4 \text{OH}^- \rightarrow \text{AlO}_2^- + 2 \text{H}_2\text{O} + 3 \text{e}^- \quad \text{(1-2)}$$

The anodic (oxidation) reactions of aluminium are to be accompanied by cathodic (reduction) reactions. The nature of these cathodic reactions depend largely on the environmental conditions, as shown in Equations 1-3 through 1-6:

In deaerated acid media:

$$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \ (\text{g}) \quad \text{(1-3)}$$

In aerated acid media:

$$4 \text{H}^+ + \text{O}_2 + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \quad \text{(1-4)}$$

In deaerated neutral media (it should be noted that this reaction is slow):

$$2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 \ (\text{g}) + 2 \text{OH}^- \quad \text{(1-5)}$$

In aerated neutral media:

$$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad \text{(1-6)}$$

1.2.2 Uniform and localised corrosion

Corrosion of a metal combines the oxidation of metal atoms to ions and the reduction of other chemical species (e.g. $\text{O}_2$ or $\text{H}^+$) [1.19, 1.20]. The oxidation and reduction reactions are defined as the anodic and cathodic reactions respectively. The electrons produced by the anodic reaction are consumed by the cathodic reaction. The anodic and cathodic reactions each form a half-cell while the combination of the two form a corrosion cell. With uniform
corrosion the anodic and cathodic reactions takes place at the same rate all over the surface and the anodic and cathodic sites are not spatially well defined. With localised corrosion these sites are spatially separated and the oxidation and reduction reactions each occur preferentially at different locations on the metal surface. Uniform and localised corrosion are schematically presented in Figure 1-2(a) and 1-2(b) respectively, in case of exposure of aluminium to an aerated electrolyte.

Figure 1-2: Schematic representation of uniform (a) and localised (b) corrosion of an aluminium based substrate in an aerated corrosive environment

1.2.3 Microstructural effects

Because of the electrochemical nature of corrosion processes, the overall corrosion potentials of different aluminium alloys are of considerable importance. Furthermore the corrosion potential relationships among the matrix and particles (i.e. precipitates, dispersoids and constituent particles of intermetallic phases) in a particular alloy may significantly influence its localised corrosion behaviour. Type of alloying element, the concentration in solid solution and in intermetallic particles as well as the spatial distribution of particles may affect both type and extent of localised corrosion [1.16]. The composition and morphology of the matrix and the intermetallic particles are a function of
the thermomechanical treatments during the preceding production steps such as casting, solidification, homogenisation, rolling or extrusion and precipitation treatment.

The corrosion potential of an aluminium alloy in a particular electrolyte is determined primarily by the composition of the aluminium-rich solid solution matrix, which constitutes the predominant area and volume fraction of the alloy microstructure. The effects of principal alloying elements on the corrosion potential of aluminium based alloys are presented in Figure 1-3.

![Figure 1-3](image)

Corrosion potentials are for high-purity binary alloys solution heat treated and quenched. 
Measured in a solution of 53 g/l NaCl plus 3 g/l H₂O₂ maintained at 25 °C.

**Figure 1-3:** Effects of principal alloying elements on the corrosion potential of aluminium alloys [1.16]

Figure 1-3 shows an increase of the corrosion potential of binary aluminium alloys when Cu, Mn, and to a lower extent Si are added, while Mg and especially Zn lead to a decrease of the corrosion potential. For each element, the significant changes that occur do so within
the range in which the element is in complete solid solution. Further addition of the same element, leading to the formation of an intermetallic particle, causes little additional change in the corrosion potential. Most commercial aluminium alloys contain more than one type of alloying element: effects of multiple elements in solid solution on the corrosion potential can be approximated by addition of the individual effects [1.16]. However the corrosion potential of the alloy is not affected significantly by intermetallic particles of microscopic size, as discussed just above, these particles frequently have corrosion potentials differing from that of the solid solution matrix in which they occur. In this way localised corrosion may be promoted due to the formation of micropolarizic cells between themselves and the matrix when exposed to an electrolyte solution or a humid atmosphere. In Table 1-1, the corrosion potentials of a range of intermetallic particles in different electrolytes are listed [1.21].

Table 1-1:  Corrosion potentials for a selection of intermetallic compounds common in aluminium alloys

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Corrosion Potential [V_{SCE}]</th>
<th>Environment</th>
<th>Aeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;Cu</td>
<td>-0.70</td>
<td>0.5 M NaCl</td>
<td>Open to air</td>
</tr>
<tr>
<td>AlCu</td>
<td>-0.49</td>
<td>0.5 M NaCl</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;Cu&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-0.36</td>
<td>0.5 M NaCl</td>
<td>Open to air</td>
</tr>
<tr>
<td>AlCu&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.32</td>
<td>0.5 M NaCl</td>
<td>Open to air</td>
</tr>
<tr>
<td>AlCu&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-0.26</td>
<td>0.5 M NaCl</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;3&lt;/sub&gt;Mg&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-1.15</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>MgZn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.96</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;CuMg</td>
<td>-0.91</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al</td>
<td>-0.76</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;6&lt;/sub&gt;Mn</td>
<td>-0.76</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;Cu</td>
<td>-0.64</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;3&lt;/sub&gt;Fe</td>
<td>-0.47</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Al&lt;sub&gt;3&lt;/sub&gt;Ni</td>
<td>-0.43</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Si</td>
<td>-0.17</td>
<td>53 g/l NaCl + 3 g/l H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Open to air</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;Si</td>
<td>-1.59</td>
<td>NaCl (no details)</td>
<td>Deaerated</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;Si</td>
<td>-1.53 to -0.68</td>
<td>3% NaCl</td>
<td>Not stated</td>
</tr>
</tbody>
</table>
Chapter 1

The values presented in this Table 1-1 should be handled with some caution. The majority of the corrosion potentials reported in [1.21] were determined from bulk intermetallic compound samples prepared in such a manner that standard electrochemical techniques could be used. Relatively few references presented in [1.21] offer detailed characterisation data to judge the quality of the bulk intermetallic compound. Factors that may degrade quality include incorrect composition, the presence of phases other than the intended intermetallic compound, and inclusion of defects such as cracks and porosity due to gas entrapment. These facts must be considered when using these corrosion potential data. A second cautionary point is that most of the corrosion potentials reported in table 1-1 are values achieved after 30-120 minutes of exposure. It may be inappropriate to use these data to account for corrosion phenomena occurring over much longer time periods. Active phases that contain copper are noteworthy examples. Immediately after exposure to aerated chloride solutions, the Al$_2$CuLi phase exhibits a corrosion potential of $-1.7$ to $-1.8$ V vs. SCE which is considerably more active than the value of $-1.1$ V vs. SCE that is attained after 20-30 minutes of exposure [1.21].

Traditionally, local corrosion processes have been attributed to the interactions between the matrix and intermetallic particles [1.22, 1.23]. Recent studies [1.24-1.27] of particle-induced corrosion indicate that the electrochemical character of intermetallic particles are not constant but can vary and may be broadly divided into particles which are cathodic or anodic with respect to the aluminium matrix [1.24, 1.25]. Schematic representations of the localised corrosion processes in case of the presence of cathodic or anodic particles are presented in Figure 1-4(a) through 1-4(d) respectively. Cathodic particles tend to promote dissolution of the (anodic) surrounding matrix, as shown in Figure 1-4(a) and may eventually lead to detachment of the particle, due to undercutting, leaving a pit in the aluminium based matrix, as shown in Figure 1-4(b). In case of an anodic particle, as shown in Figure 1-4(c), this particle is dissolved preferentially, eventually leaving a pit in the alloy surface, as shown in Figure 1-4(d). It should be noted that when the localised corrosion process proceeds the active surface area of the (cathodic) particles increases due to the dissolution of the surrounding matrix. This further increases the matrix dissolution rate accompanying the increasing cathodic activity on the particles with increasing active surface area.

The division of particles in cathodic or anodic with respect to the matrix, however, is not precise. In case an aluminium containing particle (e.g. Al$_2$CuMg) is anodic to the surrounding matrix, aluminium or other elements may dissolve preferentially from this
particle. This preferential dissolution of elements eventually leads to surface enrichment of the particle (e.g. enrichment of Cu). In this way, the electrochemical nature of such a particle may change from anodic to cathodic. Progressive local corrosion may lead to complete detachment or dissolution of particles and the formation of holes or pits. Depending on the electrolyte conditions, these pits may grow further or coalesce to form larger pits, or repassivate.

**Corrosive environment**

![Diagram](a)

**Corrosive environment**

![Diagram](b)

**Corrosive environment**

![Diagram](c)

**Corrosive environment**

![Diagram](d)

*Figure 1-4: Local dissolution of an aluminium based substrate in case of the presence of cathodic, (a) and (b), or anodic intermetallic particles, (c) and (d)*
This discussion indicates that microstructural variations, in particular type, concentration and distribution of alloying elements, in aluminium based substrates can play a very important role in localised corrosion processes. It has to be realised furthermore that not only the electrochemical nature of alloying elements determining the formation of local microgalvanic cells influences localised corrosion processes, but also the composition and structure of the surface layer/oxide is strongly influenced by the local composition of the underlying aluminium alloy. Especially particles with microscopical dimensions can influence the composition and structure of this surface layer/oxide [1.28]. Local breakdown of the surface film enables subsequent local dissolution of the metallic substrate [1.29-1.31].

The microstructure of an aluminium alloy is neither a physical constant nor fully defined by its chemical composition only but mainly depends on the complete processing route, which can result in wide variations of alloying element concentration and distribution in the matrix and in the particles, as well as particle size and spatial distribution. For this reason it can be explained that large variations in the local corrosion susceptibility among alloys with equivalent chemical composition, but apparent differences in thermo-mechanical history, have been reported.

### 1.2.4 Commercial alloys

**Designation of commercial alloys**

Aluminium mill products are those aluminium products that have been subjected to plastic deformation by hot and cold working mill processes such as rolling, extrusion and drawing, either singly or in combination, that transform cast aluminium ingot to the desired product form [1.32]. A standard system of four-digit numbers is used for the designation of wrought aluminium and its alloys. The first digit indicates the alloy series, as presented in Table 1-2.

Apart from the AA1xxx alloys, the third and fourth digits in the designation have no numerical significance but only identify the different aluminium alloys in the group. The second digit in the designation indicates alloy modifications. If the second digit in the designation is zero, it indicates the original alloy; integers 1 through 9, which are assigned consecutively, indicate minor modifications of the original alloy in alloy and/or impurity limits.
Table 1-2: Commercial aluminium alloy designation system

<table>
<thead>
<tr>
<th>Alloy series</th>
<th>Principal alloying element(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA1xxx</td>
<td>Controlled unalloyed compositions (Al ≥ 99.00%)</td>
</tr>
<tr>
<td>AA2xxx</td>
<td>Copper</td>
</tr>
<tr>
<td>AA3xxx</td>
<td>Manganese</td>
</tr>
<tr>
<td>AA4xxx</td>
<td>Silicon</td>
</tr>
<tr>
<td>AA5xxx</td>
<td>Magnesium</td>
</tr>
<tr>
<td>AA6xxx</td>
<td>Magnesium and Silicon</td>
</tr>
<tr>
<td>AA7xxx</td>
<td>Zinc</td>
</tr>
<tr>
<td>AA8xxx</td>
<td>Other elements</td>
</tr>
<tr>
<td>AA9xxx</td>
<td>Reserved for future use</td>
</tr>
</tbody>
</table>

Heat treatment of aluminium alloys

The term heat treatment, refers to any of the heating and cooling operations applied to change the mechanical properties, the microstructure or the residual stress state of a metal product [1.33]. The use of the term heat treatment is usually restricted to those specific operations employed to increase strength and hardness of aluminium alloys by precipitation hardening. These alloys are referred to as heat treatable alloys. Other types of alloys, the so-called non-heat-treatable alloys, achieve no significant strengthening by heating and cooling operations and depend primarily on cold work to increase strength. Heating to decrease strength and increase ductility is used for both types of alloys and is referred to as annealing. As microstructural changes during annealing vary with alloy type and with degree of softening desired, the annealing temperature range can vary from about 300 °C to about 450 °C, while the annealing time can vary from seconds at high temperatures to hours at low temperatures.

One essential attribute of a precipitation-hardening alloy is a temperature dependent equilibrium concentration in solid solution characterized by decreasing solubility with decreasing temperature. In this case, second-phase particles can be formed by solid-state precipitation when the alloy is cooled from above the solvus temperature. This condition is met by most binary aluminium systems, however the degree of precipitation hardening is system dependent and for the non-heat-treatable alloys considered to be non-significant, such as Al-Si and Al-Mn systems. In contrast, alloys of the Al-Cu system exhibit
significant changes. In heat treatable aluminium alloys, solid-state precipitation can take place at room temperature, which is called natural ageing. This process can be accelerated by heating the alloy to slightly elevated temperatures: this is called precipitation heat treatment or artificial ageing.

Heat treatable commercial alloys include the wrought alloys of the AA2xxx, AA6xxx and the AA7xxx series. Some of these alloys contain only Cu, or Cu and Si, as the primary strengthening alloying elements. Most of the heat treatable alloys, however, contain combinations of Mg with one or more of the elements Cu, Si and Zn. Mg combines with Cu, Si and Zn to form complex second-phase particles whose precipitation usually is faster and more pronounced than that of the simpler $\text{Al}_2\text{Cu}$ or $\text{AlZn}$ compounds.

**AA1xxx-series**

Wrought AA1xxx-series alloys conform to composition specifications that set maximum individual, combined and total alloying element concentrations present as natural impurities. The corrosion resistance of all AA1xxx-series alloys is generally high, but slightly decreases with increasing alloying element concentrations. Fe, Si and Cu are the major elements present in the alloys. The Cu and part of the Si are in solid solution. The particles in the alloys contain either Fe or Fe and Si ($\text{Al}_6\text{Fe}$, $\text{Al}_3\text{Fe}$ and $\text{Al}_{12}\text{Fe}_5\text{Si}$). The specific phases present depend on the ratio of Fe to Si and on thermal history. The microstructural particles of these phases are cathodic to the aluminium based matrix, and exposed surfaces of the particles are covered with a thinner oxide film than that covering the exposed area of the matrix. For this reason, corrosion may be initiated in the matrix surrounding the particles. The number and/or size of such local attack is proportional to the surface area fraction of the particles. Again, it should be noted that because of relatively low levels of alloying additions the corrosion resistance of the AA1xxx-series is relatively good compared to the other series.

**AA2xxx-series**

Alloys of this series of alloys, with Cu as major alloying element, are generally less resistant to corrosion than alloys of other series with lower Cu concentrations. Alloys of this type were the first heat treatable, high-strength aluminium based alloys, with structural application in the aircraft and aerospace industry.

The corrosion potential of the AA2xxx-series alloys depends largely on variations of Cu in solid solution, as shown in Figure 1-3. Furthermore, under certain circumstances, the
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corrosion potential is prone to large variation because of the presence of nonuniformities in solid solution concentration. However, the fact that the general resistance to corrosion decreases with increasing Cu concentration is primarily to be attributed to the formation of microgalvanic cells between the (cathodic) Cu-containing particles and the surrounding matrix. It has also been reported in the literature [1.16] that as corrosion proceeds, Cu ions, which initially go into solution, replate on the alloy surface to form metallic Cu cathodes. The increased \( \text{O}_2 \) and \( \text{H}^+ \) reduction reaction rate on metallic Cu and Cu-containing particles, increases the dissolution rate of the surrounding aluminium matrix.

**AA3xxx-series**

This series of alloys is generally very resistant to corrosion. The Mn is present in the solid solution matrix, as well as in submicroscopic and larger particles of \( \text{Al}_6(\text{Mn,Fe}) \) or \( \text{Al}_{12}(\text{Mn,Fe})_3\text{Si} \) phases. both phases have corrosion potentials almost the same as the matrix. These alloys are used for a wide variety of architectural, cooking and food-processing applications requiring high corrosion resistance.

**AA4xxx-series**

Elemental Si is present as second phase particles in wrought alloys of the AA4xxx-series. Si is cathodic to the aluminium solid solution matrix by several hundreds of millivolts and accounts for a considerable area fraction of most of the Si containing alloys.

**AA5xxx-series**

Wrought aluminium alloys of the AA5xxx-series have high resistance to corrosion, which accounts for their use in a wide variety of automotive applications, building products and chemical-processing equipment, as well as applications involving exposure to seawater. Alloys in which the Mg is present in amounts that remain in solid solution, or only partially precipitated as \( \text{Al}_5\text{Mg}_3 \) particles dispersed uniformly throughout the matrix, are generally as resistant to corrosion as commercially pure aluminium. The wrought alloys containing about 3% or more Mg under conditions that lead to an almost continuous intergranular \( \text{Al}_5\text{Mg}_3 \) precipitate, with very little precipitate within the grains, may be susceptible to exfoliation or stress-corrosion cracking. Special tempers have been developed for these alloys containing higher amounts of Mg to promote the formation of this precipitate type within the grains, thus decreasing this susceptibility.
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In the AA5xxx-series alloys containing Cr, this element is present as a submicroscopic precipitate, Al\textsubscript{12}Mg\textsubscript{2}Cr. Mn in these alloys is present as part of the submicroscopic or larger particle Al\textsubscript{6}(Mn,Fe). Both particle types do not adversely affect the corrosion resistance of these alloys.

**AA6xxx-series**

The combination of moderately high strength and very good resistance to corrosion makes the heat treatable wrought alloys of the AA6xxx-series suitable for application in a.o. building, automotive, maritime and process-equipment industry. In solid solution or as submicroscopic precipitate, the Mg\textsubscript{2}Si phase has a negligible effect on the corrosion potential of the alloy. Because these alloys normally are used as in the precipitated condition, no detrimental effects derive from the major alloying elements Mg and Si. When the Mg\textsubscript{2}Si particles come in contact with an aqueous environment, preferential dissolution of the Mg component can take place, leaving an electrically insulating SiO\textsubscript{2} layer on the surface [1.15, 1.34]. Also additions of Cr, Mn or Zr, for control of grain structure do not affect the corrosion resistance. Copper additions increasing the strength of the alloys are limited to small amounts to minimise effects on the corrosion resistance. In general, the level of corrosion resistance decreases somewhat with increasing copper content.

**AA7xxx-series**

These alloys contain major additions of Zn along with Mg or Mg plus Cu in combinations that develop various levels of strength. Those containing Cu have the highest strengths and are commonly used as primary construction materials, principally in aircraft applications. The AA7xxx wrought alloys are anodic to 1xxx wrought alloys, because of their high Zn content. Resistance to general corrosion of the Cu-free AA7xxx alloys is good, approaching those of wrought AA3xxx, AA5xxx and AA6xxx alloys. The Cu-containing AA7xxx alloys, such as AA7075, have lower resistance to general corrosion than those of the same series that do not contain Cu. All AA7xxx alloys are more resistant than AA2xxx alloys, but less resistant than wrought alloys of other groups.
1.3 Filiform corrosion of aluminium alloys

1.3.1 Initiation

In the literature it has been stated that the following conditions are to be met for filiform corrosion to occur [1.1-1.3, 1.35, 1.36]:

- The presence of coating defects
- Contamination of the coating-substrate interface with salts
- An atmosphere of high relative humidity

These conditions cover both the initiation and propagation stages of filiform corrosion and need not necessarily apply at the same time [1.12]. The condition of a permeable coating for O₂ and H₂O, as often stated in the literature [1.1-1.3, 1.35, 1.36], is only valid in the very early stages of filiform corrosion initiation in case of coverage with an intact coating of an area with local loss of adhesion [1.12]. The (possible) initiation steps are schematically presented in Figure 1-5, from osmotic blistering underneath an intact coating, e.g. due to salt contamination, towards the first stages of the formation of a differential aeration cell after subsequent rupture of the organic coating.

Figure 1-5(a) shows O₂ and H₂O transport through a locally bad adhering intact coating. Such blisters may be the result of bad curing or handling of the organic coating or poor final rinsing after application of a pretreatment layer. Salt particles may be left at the coating-substrate interface preventing total wetting of the surface by the organic coating. The blisters underneath intact coatings may grow due to osmosis mainly depending on the hygroscopic properties of the salt particles at the coating-substrate interface. The osmotic blistering process occurs when the organic coating is permeable for H₂O, but strongly retarding for ionic species, which is the case for most organic coatings [1.12]. The organic coating thus behaves as a membrane. Water molecules at the coating-substrate interface will weaken and finally break the chemical adhesive bonds between the polymer and the substrate surface resulting in (further) adhesion loss. Swelling of the coating due to water absorption of the organic coating, resulting in the build up of interfacial stresses, is a secondary effect promoting adhesion loss.
Figure 1-5: Initiation mechanism of filiform corrosion on aluminium based substrates. (a) and (b) cover the consecutive phenomena occurring underneath (bad adhering) intact coatings, while (c) is the mechanism in the presence of a coating defect or after rupture of the organic coating as the next stage after (b).
The transport of $O_2$ and $H_2O$ through the organic coating and the presence of aggressive anions such as $Cl^-$ will result in blister growth, electrolyte formation and the occurrence of corrosion reactions in the blister, as shown in Figure 1-5(b).

On a macro-scale, these reactions will occur randomly throughout the blister. When analysed in more detail these corrosion reactions will be influenced by heterogeneities in the natural oxide / pretreatment layer and underlying substrate, as is the case for other types of localised corrosion. The corrosion process will indirectly influence the delamination at the edge of the blister by increasing the electrolyte concentration and herewith enlarging the driving force for the osmotic process. The build up of corrosion product and the osmotic pressure in the blister will finally lead to coating failure as presented in Figure 1-5(c). This rupture of the organic coating is a necessary condition for the formation of a differential aeration cell as now will be discussed. In the case of a coating defect being present, it can be shown that for aluminium based substrates the main oxygen transport path is through the corrosion products [1.3, 1.12]. This preferential oxygen transport path leads to the formation of such a differential aeration cell where oxygen is mainly reduced at the (oxygen-rich) center of the blister and the dissolution of aluminium occurs at the (oxygen-deficient) edges of the blister. Such separation of the cathodic site from the anodic site as is the case for filiform corrosion on coated aluminium based substrates is defined as anodic undermining. The consecutive chemical and electrochemical reactions occurring during initiation of filiform corrosion will now be described in more detail.

As discussed in Section 1.2, local breakdown of the protective overlying natural oxide / pretreatment layer enables local dissolution of the aluminium based substrate. Due to interaction with water from the environment, the outer surface layer of the aluminium oxide layer may be hydrated to form $Al_2O_3\cdot H_2O$ (AlOOH, boehmite) and $Al_2O_3\cdot 3 H_2O$ ($Al(OH)_3$, gibbsite), as shown in Equations (1-7) and (1-8):

$$Al_2O_3 (s) + H_2O \leftrightarrow 2 AlOOH (s) \quad (1-7)$$

$$AlOOH (s) + H_2O \leftrightarrow Al(OH)_3 (s) \quad (1-8)$$

The passive aluminium (hydr)oxide layer will breakdown in the presence of chlorides according to the following four consecutive steps [1.15, 1.37]:

- Adsorption of $Cl^-$ on the aluminium (hydr)oxide layer
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- Chemical reaction of Cl\(^-\) with the precipitated aluminium hydroxide, according to the anion exchange reactions as shown in Equations (1-9) through (1-12)
- Thinning of the aluminium oxide layer by dissolution
- Direct attack of the exposed aluminium substrate

The chemical reactions of Cl\(^-\) with the precipitated aluminium hydroxide are:

\[
\text{Al(OH)}_3 + n \text{Cl}^- \leftrightarrow \text{Al(OH)}_{3-n}\text{Cl}_n (s) + n \text{OH}^- \quad (1-9)
\]

With \( n = 1, 2, 3 \) consecutively

Or, in acid and neutral chloride containing solutions the following chemical reactions may occur consecutively:

\[
\text{Al(OH)}_3 + \text{Cl}^- + \text{H}^+ \leftrightarrow \text{Al(OH)}_2\text{Cl} (s) + \text{H}_2\text{O} \quad (1-10)
\]

\[
\text{Al(OH)}_2\text{Cl} + \text{Cl}^- + \text{H}^+ \leftrightarrow \text{Al(OH)}\text{Cl}_2 (s) + \text{H}_2\text{O} \quad (1-11)
\]

\[
\text{Al(OH)}\text{Cl}_2 + \text{Cl}^- + \text{H}^+ \leftrightarrow \text{AlCl}_3 (s) + \text{H}_2\text{O} \quad (1-12)
\]

These reactions show that stable and soluble transitory aluminium hydroxychloride complexes are formed after adsorption of chloride ions at the outer surface and a competitive interchange starts between the hydroxide ligands and the chloride ions. The chloride ions are regenerated after dissolution of the transitory hydroxychloride compounds and thus only a relatively limited and constant amount of chloride ions can result in progressive attack of the protective layer [1.15].

1.3.2 Propagation

After initiation of a circular blister or initiation from an edge or scratch defect and the establishment of a differential aeration cell, the transition from circular lateral growth to more uni-directional thread-like type of corrosion may take place. Filiform corrosion propagation on aluminium based substrates occurs via anodic undermining. The anodic site is located at the very tip of the filament and the cathodic site is spatially separated and
located at the back of the head or at the front of the area where corrosion products are deposited [1.15], as shown in Figure 1.6.

![Diagram showing filiform corrosion mechanism](image)

\[ \text{Head} \quad \text{Tail} \]

\[ \text{H}_2\text{O} , \text{O}_2 \]

\[ \uparrow \text{ = Anodic Al dissolution reaction} \]
\[ \blacktriangledown \text{ = Cathodic O}_2 \text{ reduction reaction} \]
\[ \circ \text{ = Cathodic H}^+ \text{ reduction reaction (H}_2\text{ bubbles)} \]

\[ (a) \]

\[ \text{Head} \quad \text{Tail} \]

\[ \text{Corrosion products} \]
\[ \text{Coating defect} \]

\[ \text{Anodic site} \quad \text{Cathodic site} \]

\[ (b) \]

**Figure 1-6:** Propagation mechanism of filiform corrosion on aluminium based substrates. (a) shows a longitudinal section of a filament, while (b) is a top view representation.

The transition between the head and the tail of the filament, filled with corrosion products, of the filament is rather vague. The corrosion products in the tail may vary from wet or gel-like near the head to dry further down the tail [1.12, 1.15].
At the anodic site, aluminium dissolution takes place according to Equation 1-13. Due to hydration of aluminium ions, local acidification of the anolyte takes place and a secondary cathodic reaction, the reduction of hydrogen ions as shown in Equation 1-14, can occur:

$$\text{Al} + 2 \text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Al(OH)}_2\text{Cl} + 2 \text{H}^+ + 3 \text{e}^- \quad (1-13)$$

$$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \text{(g)} \quad (1-14)$$

In literature [1.2, 1.10, 1.13, 1.35] gas evolution is often observed in the tip of the filament head and these bubbles are taken to be hydrogen bubbles from such reaction. The hydration of aluminium ions is reported to be a complex series of intermediate steps with the formation of hydroxychloride complexes towards stable corrosion products filling the filament tail [1.14, 1.15]. Preceding the electrochemical reactions shown above, the acid chloride containing anolyte provides the necessary condition for chemical breakdown of the protective coating-substrate interface (i.e. natural oxide or pretreatment layer), exposing the substrate microstructure. This process, as discussed in the preceding section, includes the chloride release from transitory hydroxychloride complexes providing electroneutrality conditions in the anolyte and continuous participation of a more or less constant number of chloride ions in the substrate surface attack. However, some entrapment of chloride in the corrosion product filled filament tail could contribute to a stagnation of filament growth rate after considerable exposure times [1.2, 1.11, 1.13, 1.15], in addition to a decrease of oxygen concentration gradient with increasing filament lengths [1.12, 1.15, 1.38].

At the cathodic site the primary cathodic reaction, the reduction of oxygen, takes place:

$$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad (1-15)$$

Inherent to the anodic undermining mechanism for filiform corrosion on aluminium based substrates, there is a general consensus that oxygen is mainly transported through the tail of the filament. There is little agreement on the main transport path for water towards the cathodic site. On one hand, the main transport path is reported to be through the organic coating: Slabaugh et al. [1.2] reported the filiform corrosion propagation rate to be depending on the coating permeability and Lenderink [1.12] suggested that the presence of dry corrosion product in the filament tail would contradict water transport through the porous tail. On the other hand, Leth-Olsen [1.13] rules out the possibility of a main water
transport through the coating based on the observations that filiform corrosion is also reported to occur under (impermeable) metal-plate coatings [1.1] and to grow undisturbed underneath a part of a coated specimen covered by an (impermeable) aluminium foil. It can also be argued that a confined amount of water could be sufficient to keep the filiform corrosion process going by regeneration of $H_2O$ molecules during filiform corrosion propagation.

1.3.3 Influencing parameters

Filiform corrosion on coated aluminium alloys is a complex phenomenon involving influences of the environment, the organic coating, the coating-substrate interface (i.e. the natural oxide or pretreatment layer) and the substrate (surface) microstructure. It must be realised that separation of individual effects is difficult as effects of these substructures are interactively coupled.

Many recent investigations into the mechanism of filiform corrosion [1.11-1.15], coating [1.11, 1.39, 1.40] and pretreatment effects [1.8, 1.10-1.15, 1.41-1.44] on filiform corrosion of coated aluminium alloys have resulted in a better understanding of the general and local filiform corrosion mechanism on aluminium. The general conclusions from these studies indicate that proper pretreatment, independent of the organic coating applied, can significantly reduce substrate susceptibility and even totally protect aluminium alloys against filiform corrosion. In contrast, the tested organic coatings are incapable of preventing filiform corrosion to occur on susceptible aluminium alloys which is in line with the present insights into the filiform corrosion mechanism. Due to the extensive and detailed recent reviews of the present insights into the mechanism of filiform corrosion, environmental and coating effects, the reader is referred to these publications [1.10-1.15] and these topics are left out of further discussion in this thesis.

Aim of the present investigation is to gain more insight into the effect of microstructural variations in the substrate (surface) of aluminium alloys. The available literature about microstructural effects on filiform corrosion is reviewed and discussed in the next section. Conversion coatings are commonly used on aluminium based surfaces in order to improve the corrosion resistance of the metal, masking microstructural effects on corrosion susceptibility, and establish an adhesive base for organic coatings. When examining the effect of microstructural variations both a minimal but reproducible pretreatment (e.g. controlled degreasing) and technically well proven pretreatments are of particular interest.
and taken into account during the present investigations. For this reason also the available literature on pretreatment effects is briefly reviewed in section 1.3.5.

1.3.4 Microstructural effects

Besides recent studies of Leth-Olsen et al. [1.13, 1.45-1.49] and parallel investigations by Afseth [1.14], little systematic research has been performed into the more exact role of microstructural variations in the substrate (surface). There is a general consensus that the chemical composition of the substrate under investigation plays an important role in the filiform corrosion susceptibility [1.8-1.14, 1.50]. Some of these studies [1.9, 1.50] propose that filiform corrosion susceptibility of certain aluminium alloys can be restricted and controlled by definition of compositional specifications. However, it has to be realised that the filiform corrosion susceptibility is not only a function of the chemical composition but also largely depends on the thermo-mechanical history of the alloys under investigation [1.11-1.14]. For this reason, large variations among alloys with the same chemical composition but apparent different thermo-mechanical histories are reported in the literature. Reduction of the substrate susceptibility to filiform corrosion can be achieved by removal of the outer substrate surface layer (e.g. by caustic etching) [1.2, 1.11-1.14].

Olsen [1.13] showed in his studies on Al-Mn based (AA3005) and Al-Fe based (AA8006 and an unidentified alloy X) that preferential microstructural changes in the outer metal surface layer during high temperature annealing of corrosion resistant substrates resulted in drastic deterioration of their filiform corrosion susceptibility. Filiform corrosion, microstructural and electrochemical studies were exerted to show that the very refined grain structure of the outer surface layer, consisting of subgrains in the size range 20 to 200 nm, was confined to within about 1 μm from the metal surface and this outer surface proved to be electrochemically more active than the underlying bulk substrate. By cold-rolling also a grain refined surface layer was found to be formed, but this layer did not result in surface activation and increased filiform corrosion susceptibility. Surface activation by annealing of etched surfaces, together with the results of the cold-rolled surfaces indicate that grain refined surface layers alone are not responsible for the increased surface activity compared to that of the underlying bulk. The analytical techniques employed could not identify the particular microstructural changes causing the increased filiform corrosion susceptibility after high temperature annealing. An obvious method for protection of substrates against filiform corrosion was proposed involving removal of the
outert active surface layer by etching or other pretreatment directly prior to coating application.

Investigating the rolled aluminium alloys AA3005 and AA5754, Afseth [1.14] concluded that filiform corrosion properties of rolled aluminium alloys are predominantly controlled by the microstructural characteristics of the very outer, thin (~1 μm), heavily deformed surface layer, resulting from large surface shear deformation in the rolling process. A higher corrosion susceptibility of the surface layers was attributed to higher densities of secondary precipitated intermetallic particles combined with lower solid solution content of electrochemically noble alloying or impurity elements compared to those in the underlying bulk. Such formation of a highly susceptible surface layer results in a preferentially superficial mode of attack, causing rapid filiform corrosion propagaton. In particular, for the AA3005, exposure to high temperatures, as experienced during hot rolling and annealing, in excess of 350 °C caused preferential precipitation of intermetallic particles in the heavily deformed outer surface layer. Preferential attack of the surface layer was therefore attributed to the higher density of fine intermetallic particles and a lower level of manganese in supersaturated solid solution. Variations in the Fe content, within the compositional limits of AA3005, did not significantly affect the filiform corrosion while Cu additions resulted in higher filiform corrosion susceptibility for as rolled materials. In all cases a high filiform corrosion resistance was found when cleaning practises were applied involving removal of a significant amount of metal from the surface. These results again confirm that the chemical composition only partially determines the filiform corrosion susceptibility and the microstructural state and surface condition of the alloys are at least as important. The AA5754 alloy did not show a similar significant sensitivity to heat treatment, which can be attributed to the lower Fe and Mn content in this alloy. Studies of simple binary model alloys confirmed that filiform corrosion takes place resulting from the formation of microgalvanic coupling between the aluminium rich matrix and electrochemically more noble second phase particles. These particles may be intermetallic compounds, such as iron aluminides, or as in the case of Cu containing alloys, localised surface enrichments of Cu on the surface, due to preferential attack during corrosion.

1.3.5 Pretreatment effects

As indicated in the previous sections, surface preparation and pretreatment procedures
largely influence the filiform corrosion susceptibility of coated aluminium alloys [1.8, 1.10-1.15, 1.41-1.44]. A wide variety of pretreatment layers is commonly used as the intermediate layer between the organic coating and the aluminium alloy, in order to improve corrosion resistance and an suitable base for adhesive bonding. The aim of the investigations presented in this thesis is to elucidate the effects of microstructural variations in the substrate (surface). Hence only a limited number of pretreatments such as degreasing, deoxidising, chromating and cerating were considered. For this reason, the present review of effects of pretreatment focusses on these pretreatment procedures. For more detailed information the reader is referred to [1.8, 1.10-1.15, 1.41-1.44].

The effect of microstructural variations in the substrate surface is tested in its most pure form when tested in the degreased only condition. It serves as a reference when evaluating different pretreatments. However, one of the goals of the application of a specific pretreatment layer is to provide a proper adhesive base for the organic coating, so particular care has to be taken when applying an organic coating on a degreased only sample to avoid bad adhesion, leading to blister formation and front corrosion rather than filiform corrosion.

A deoxidising step is usually incorporated in standard pretreatment procedures prior to coating such as anodising or the application of chemical conversion coatings such as chromate conversion coatings. In the previous section it was shown that investigations indicate that the filiform corrosion susceptibility of aluminium alloys decreases with the removal of the outer surface layer hereby exposing the (less electrochemically active) underlying bulk material to the corrosive environment (e.g. by extensive etching or deoxidising) [1.2, 1.11-1.14].

Chromate conversion coatings are commonly used on aluminium based surfaces in order to improve the corrosion resistance of the metal and establish an adhesive base for organic coatings [1.51]. The chromate ion is an excellent corrosion inhibitor and is widely used for chromate conversion coatings and in paint pigments. Studies have found an increase of the filiform corrosion resistance of coated substrates compared to degreased only samples [1.11, 1.12]. Hexavalent chromium leaching out of the amorphous chromate film and consequently being reduced to insoluble trivalent chromium at flaws in the coating, hence inhibiting the substrate surface from further corrosion is reported to be the protecting mechanism of the chromate conversion coatings [1.13, 1.51]. On the other hand, if the chromate conversion coating is preheated to temperatures above 60 °C, e.g. during paint
curing, the hexavalent chromium is rendered insoluble and immobile and the corrosion inhibition effect is reduced.

Notwithstanding their good protective properties, it has been recognised for some time that chromates are both highly toxic and carcinogenic [1.52]. As a result of this toxicity, the concentration levels of chromate allowed in the workplace are now regulated by government agencies and users of chromate containing materials are being warned of the possible health dangers. An interesting modern alternative chromium free chemical treatment, using solutions containing cerium compounds [1.53-1.61], has been reported to be successful in the prevention of localised corrosion of aluminium and its alloys. The formation of the cerium oxide conversion coating is reviewed by Hinton et al. [1.61]. This mechanism has the local pH rising at cathodic sites across the alloy surface, e.g. intermetallic particles, as a result of cathodic reactions such as the reduction of oxygen or hydrogen preferentially occurring at these sites. When the pH reaches a level at which the solubility product of hydrated cerium oxide is exceeded, it precipitates. In this way, coalescence of isolated islands of the oxide results in coverage of the surface. Although no specific data concerning the effect of the presence of a cerium oxide conversion coating on filiform corrosion susceptibility are available, its corrosion protection ability is attributed to the suppression of the cathodic oxygen reduction reaction. This suppression in aerated solutions is believed to occur because the hydrated cerium oxide film creates a barrier to either the oxygen supply or electron supply from the underlying metal. Both are necessary reactants for oxygen reduction at cathodic sites. This suppression of the cathodic half of the corrosion reaction retards the overall corrosion rate [1.61].

1.4 Research approach

Having presented the present insights into filiform corrosion on aluminium and microstructural effects on (filiform) corrosion in particular in this literature review, it is clear that, especially due to the many parameters involved, the exact influencing mechanisms of the relevant factors for the filiform corrosion process have not been established unambiguously yet and are still subject of discussion.

Aim of the present investigation is the determination of the effect of microstructural variations in the substrate (surface) of aluminium based alloys, also taking into account pretreatment effects on the filiform corrosion properties. Generally, the influence of
alloying elements can be investigated by determining the filiform corrosion properties of technical aluminium alloys, using a statistical analysis of the results of outdoor exposure and accelerated tests. The number of initiations and average filament lengths can be related to general alloy composition and temper conditions. Such an approach yields valuable results, but a disadvantage of this procedure is the fact that important information about the initial local microstructure of the substrate after filiform corrosion attack is lost. In addition to such filiform corrosion tests and post-mortem microstructural analysis, a contribution to more insight into the mechanism of filiform corrosion and the microstructural effects is made in the present investigations by analysis of the filiform corrosion properties of well-defined and reproducible model substrates, containing synthetic defects. Also electrochemical measurements are correlated with accelerated filiform corrosion tests in this thesis. Hence, this study combines a fundamental and mechanistic investigation as well as a practical approach to filiform corrosion of model substrates and commercial alloys.

Chapter 2 deals with the analysis of accelerated filiform corrosion tests performed on binary Al-Cu, Al-Mg, Al-Si and Al-Zn model alloys, a ternary Al-MgSi alloy and on two commercial alloys, AA2024-T351 and AA7075-T651, with variations of composition and surface treatments. The surface treatments cover simple degreasing, chromate and cerium based treatments. Both microstructural and pretreatment effects are discussed. While the detailed examination of the filiform corrosion rate as a function of the substrate composition and the surface pretreatment applied yields valuable results, it does not provide explanations for observed dependencies. The underlying mechanisms for filiform corrosion can only be further elucidated by performing electrochemical measurements in media characteristic for the corrosion process studied, as presented in Chapter 3. To this aim potentiodynamic polarisation measurements in synthetic anolyte and catholyte media, which are characteristic for the local anodic and cathodic sites in the filaments on the aluminium substrates, are performed on six of the most interesting alloys. A mechanistic study of filiform corrosion attack on AA2024-T351 and chemical analysis of electrolytes and corrosion products are presented in Chapter 4. To this aim several physical and chemical characterisation techniques on a macro- and microscopic scale were used to elucidate the general and local mechanism of filiform corrosion on aluminium. These techniques include Scanning Kelvin Probe measurements, time lapse video analysis during accelerated exposure tests, pH measurements in the local solute at the filament tip and SEM/EDX analysis of the filiform corrosion product and attack.
To study the effect of inhomogeneities in the substrate surface, copper- and magnesium-rich synthetic defects were generated on the surface of AA1060-H24 sheet, as outlined in Chapter 5. One set of samples with copper-rich defects were generated by sputtering of tracks of alloying elements and a thermal treatment to stimulate diffusion of copper in the aluminium matrix. Another set of samples contained copper pens inserted in drilled holes. The magnesium-rich defects were produced by ion implantation. Also the results of the investigation into surface texture effects on filiform corrosion propagation are presented in this chapter.

Aim of a unique set of experiments performed in collaboration with an industrial extrusion plant presented in Chapter 6 is the determination of the combined effect of heat treatment before and after the extrusion on the filiform corrosion properties of AA6005A and AA6063 and the surface pretreatment before application of the organic coating. The morphology and distribution of the Mg2Si particles in these alloys are varied by a wide range of thermal treatments before and after the industrial extrusion process. In addition, potentiodynamic polarisation measurements are performed on post-extrusion heat treated AA6063 alloys.

REFERENCES

1.5 H. LEIDHEISER jr., *Corrosion* 38 (1982) p.374
1.7 Filiform Corrosion, Report VOM (Vereniging voor Oppervlaktebehandelingen van Materialen), The Netherlands (1993)


1.13 H. LETH-OLSEN, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1996)

1.14 A. AFSETH, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1999)


Introduction

p. 531


1.30 Z. SZKLARASKA-SMIALOWSKA, Corrosion 27 (1971) p. 223


1.36 H. KAESCHE, Werkstoffe und Korrosion 11 (1959) p. 668

1.37 R.T. FOLEY, Corrosion 42 (1986) p. 277


1.43 J.E. PIETSCHMANN and H. PFEIFER, Aluminium 70 (1994) p. 82


Chapter 1


1.52 D.J. McCOY, Proceedings 2nd AESF/EPA Chromium Colloquium Miami, FL, February 1990


In this chapter, accelerated filiform corrosion exposure tests are analysed, which are performed on binary Al-Cu, Al-Mg, Al-Si and Al-Zn model alloys, a ternary Al-MgSi alloy and on the two commercial alloys, AA2024-T351 and AA7075-T651, with variations of composition and surface treatments. The surface treatments cover simple degreasing, chromate and cerium based treatments. Both microstructural and pretreatment effects are discussed.

2.1 Introduction

As presented in Chapter 1, filiform corrosion is a complex phenomenon involving influences of the environmental conditions, the organic coating, the coating-substrate interface and the substrate surface. Due to the many parameters involved, the relevant factors for filiform corrosion have not been established unambiguously yet [2.1].
Aim of the present investigation is the determination of the effect of microstructural variations in aluminium based substrates as well as pretreatment effects on the filiform corrosion properties. The composition and structure of the surface layer/oxide is strongly influenced by the local composition of the underlying aluminium alloy. Especially precipitates and dispersoids with microscopical dimensions can influence the composition and structure of this surface layer/oxide [2.2]. The composition and morphology of the constituent particles are a function of the thermomechanical treatments during the preceding production steps such as casting, solidification, homogenisation, extrusion and precipitation.

Traditionally, local corrosion processes have been attributed to successive interactions between the alloy matrix and clustered particles [2.3,2.4]. Local breakdown of the surface film permits subsequent local dissolution of the metallic substrate [2.5-2.7]. Such an explanation is implicitly supported by the absence of reports on filiform corrosion on superpure aluminium.

Recent studies [2.8-2.12] of particle-induced corrosion indicate that the electrochemical characters of constituent particles can vary and may be broadly divided into particles which are cathodic or anodic with respect to the aluminium matrix. Observations [2.8,2.9] show that anodic particles are likely to be dissolved preferentially, whereas cathodic particles tend to promote dissolution of the surrounding matrix. The characterisation of these particles in this manner, however, is not precise. Because of possible preferential dissolution of particular constituent phases from anodic particles and redeposition of relatively cathodic metallic phases, such as Cu, from anodic particles back onto the alloy surface during corrosion, the electrochemical nature of particles may change during the corrosion process and most of the particles tend to behave cathodically and promote matrix dissolution. However, very little systematic research into the effects of variations of the composition and microstructure of aluminium alloys on the filiform corrosion properties has been performed. To study the effect of single alloying element additions of Si, Mg, Cu and Zn, eleven binary model aluminium alloys have been investigated during the present research. In addition, one ternary Al-MgSi model alloy and the two typical aircraft aluminium alloys AA2024-T351 and AA7075-T651 have been investigated.

As filiform corrosion not only depends on the substrate but also on the coating and on the surface pretreatment [2.1], these factors were kept constant or were set to three very different levels respectively. By choosing an air-drying coating system, microstructural
Filiform corrosion of binary, ternary and technical aluminium alloys

changes taking place during curing at elevated temperatures can be avoided and the effect of the microstructure in its as delivered state can be determined. When examining the effect of surface pretreatment both a minimal but reproducible pretreatment (controlled degreasing) and technically well proven pretreatments are of particular interest. Chromate conversion coatings are commonly used on aluminium based surfaces in order to improve the corrosion resistance of the metal and establish an adhesive base for organic coatings [2.13]. The chromate ion is an excellent corrosion inhibitor and is widely used for chromate conversion coatings and in paint pigments. However, it has been recognised for some time that chromates are both highly toxic and carcinogenic [2.14]. As a result of this toxicity, the concentration levels of chromate allowed in the workplace are now regulated by government agencies and users of chromate containing materials are being warned of the possible health dangers. An interesting modern alternative chromium free chemical treatment, using solutions containing cerium compounds [2.15-2.18], has been reported to be successful in the prevention of localised corrosion of aluminium and its alloys. The positive effect of cerium has been attributed to the inhibition of reduction reactions at cathodic sites, due to the formation of a protective cerium oxide layer on top of the aluminium substrate [2.19-2.22].

While a detailed examination of the filiform corrosion rate as a function of the substrate composition and the surface pretreatment applied yields valuable results, it does not provide explanations for observed dependencies. The underlying mechanisms for filiform corrosion can only be found by performing electrochemical measurements in media characteristic for the corrosion process studied. To this aim potentiodynamic polarisation measurements in synthetic analyte and catholyte media are performed on six of the most interesting alloy systems. The results of this correlation analysis are presented in Chapter 3.

2.2 Experimental

In this section, the base material, pretreatment and coating procedures, as well as the filiform corrosion test set-up and analysis details are discussed respectively.

2.2.1 Base material

Eleven binary and one ternary cold-rolled aluminium model alloys were examined. The
composition and alloy codes are listed in Table 2-1. All alloys have been DC cast as 20x7.5 cm blocks on a 99.998% base, scalped, homogenised 16h at 465 °C, hot-rolled to 15-20 mm, reheated 1h at 465 °C, hot rolled to 6 mm, cold-rolled to 4 mm, solution heat treated at 550/650 °C followed by a cold water quench, cold rolled to 1.1-1.2 mm and flattened in a hot press at 225 °C pressing plate temperature for 12 mins. The dimensions of the specimens are L x LT x T= 70 mm x 60 mm x 1.1-1.2 mm.

**Table 2-1:** Composition and alloy code of binary and ternary model alloys

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Alloying concentration [wt-%]</th>
<th>Alloy code</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.11</td>
<td>Al-0.11Si</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>Al-0.21Si</td>
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<tr>
<td></td>
<td>4.07</td>
<td>Al-4.07Si</td>
</tr>
<tr>
<td>Mg</td>
<td>0.44</td>
<td>Al-0.44Mg</td>
</tr>
<tr>
<td></td>
<td>3.06</td>
<td>Al-3.06Mg</td>
</tr>
<tr>
<td>Mg and Si</td>
<td>2.46 Mg and 1.40 Si</td>
<td>Al-2.46Mg1.40Si</td>
</tr>
<tr>
<td>Cu</td>
<td>0.20</td>
<td>Al-0.20Cu</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>Al-1.00Cu</td>
</tr>
<tr>
<td>Zn</td>
<td>0.19</td>
<td>Al-0.19Zn</td>
</tr>
<tr>
<td></td>
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<td>Al-0.48Zn</td>
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<td>Al-0.97Zn</td>
</tr>
<tr>
<td></td>
<td>2.09</td>
<td>Al-2.09Zn</td>
</tr>
</tbody>
</table>

In addition, two typical aircraft aluminium alloys AA2024-T351 and AA7075-T651 are studied. The dimensions of these specimens are L x LT x T= 76 mm x 128 mm x 1.6 mm.

### 2.2.2 Pretreatment and coating

For each of the alloys, the following pretreatments were applied prior to coating with polyurethane. It is important to note that none of the conditions of application of these pretreatments had been optimised for maximum corrosion protection and coating adhesion before the study commenced. Prior to the surface treatment, all specimen surfaces were carefully cleaned with ethanol.
*Filiform corrosion of binary, ternary and technical aluminium alloys*

**Degreasing**

Immersion for 10 minutes in Brulin Formula 815 GD (alkaline cleaner) at 60°C, followed by a cold water rinse in running tap water for 5 minutes.

**Chromate Conversion Coating**

A second set of specimens were chromated according to the following procedure:
- Degreasing in Brulin Formula 815GD, as above.
- Degreasing by immersion for 4 minutes in Parker Amchem Ridoline 53 (silicated alkaline cleaner), followed by a cold water rinse for 2 minutes.
- Deoxidisation by immersion for 10 minutes in Parker Amchem Deoxidiser #4 at room temperature, followed by a cold water rinse for 2 minutes.
- Chromate conversion coating by immersion in an ‘Alodine 1200’ solution in accordance with product data sheets, followed by a cold water rinse for 5 minutes. For all systems the chromating time was set to 2 minutes except for the technical alloys and the Al-Cu alloys which were chromated for 1 minute.

**Cerate Conversion Coating**

The third set of samples were cerated [2.19] according to the following procedure:
- Degreasing and deoxidisation as above for chromate conversion coating.
- Cerating at pH 2.00±0.05 at 45°C by immersion, followed by cold water rinse for 5 minutes. For all alloys the cerating time was set to 5 minutes except for the commercial alloys and the Al-Cu alloys which were cerated for 1 minute.

Following the pretreatment, an air-drying clear flexible polyurethane coating was spray deposited in two stages with a mean dry coating thickness of 42 μm in total (standard deviation 4 μm).

2.2.3 **Filiform corrosion test set-up and analysis**

The coating defect was applied by scribing through the polyurethane coating, perpendicular to the rolling direction with a scalpel, just before the initiation procedure. The filiform corrosion test was carried out according to specification DIN65472 [2.23], with the modification of an initiation time above hydrochloric acid vapour of only 15 minutes instead of 1 hour. The total exposure time was 1000 hours. The degree of filiform corrosion
Chapter 2

was then determined using optical microscopy for quantifying the density and average length of the filaments. A manual procedure was used to determine the characteristic data but good care was taken in standardizing the evaluation. Per model alloy investigated, a total scratch length of 50 mm for the degreased samples and 100 mm for the chromated and cerated samples was examined. For the AA2024-T351 and AA7075-T651 the total examined scratch length was 100 mm for the degreased samples and 200 mm for the chromated and cerated samples. Both sides of the scratch were treated separately. The filiform corrosion initiation characteristics are defined as the site density, which is the number of filaments per scratch length. The propagation properties are defined by the average filament length per specimen, with a resolution of 0.5 mm. The total attack is defined as the corrosion number, which is equal to the site density multiplied by the average filament length.

2.3 Results and discussion

For all binary, ternary and commercial aluminium alloys the values of the site density, average filament lengths and corrosion numbers after 1000 hours of accelerated exposure are presented in Figures 2-1, 2-2 and 2-3 respectively.

In all experiments filiform corrosion behaviour was observed except in the case of the experiments on degreased AA2024-T351 and AA7075-T651, where a form of front corrosion was observed and the calculated filiform corrosion characteristics are rough indications only.

2.3.1 Site density

Figure 2-1 indicates large differences in filament site density between the various alloy systems and surface pretreatments. A maximum site density of ~2 filaments per mm was obtained for the degreased Al-1.00Cu alloy, whereas a minimum site density down to ~0.01 per mm was obtained for chromated and cerated Al-Zn alloys. When evaluating the site density data of the binary alloy system it is clear that the average site density decreases in the order Al-Cu, Al-Si, Al-Zn, Al-Mg. The trend is more or less independent of the surface pretreatment applied, however the chromated and cerated Al-Zn alloys show an exceptionally good resistance to filiform initiation, with the exception of the cerated Al-2.09Zn alloy. The reason for this not known. A further observation is that for each binary
alloy system the site density increases with increasing solute content. This trend is particularly clear for the degreased samples. For the chromated and cerated samples the site density was too low to determine such a relation with any statistical significance but the data would not contradict such a conclusion.

Figure 2-1: Site density after 1000 hours of accelerated filiform corrosion test exposure for three pretreatments. The alloy codes are listed in Table 2-1.

Chromating proves to be a very effective way to reduce the filiform corrosion initiation characteristics significantly for all tested substrates. There is still some attack on the chromated AA2024-T351, AA7075-T651 and the Al-Cu binary alloys, but it has to be realized that these samples have only been chromated for 1 minute, compared to the others which have been chromated for 2 minutes. The effectiveness of cerating is expressed in a lower site density for all tested substrates with the exception of the Al-2.09Zn and the ternary Al-2.46Mg1.40Si alloys. The pretreated AA2024-T351 and AA7075-T651 alloys show equivalent filiform initiation susceptibility with site densities of ~1.05 and ~0.85 filaments per mm for the chromated and cerated samples respectively.
2.3.2 Average filament length

When analysing the average filament lengths for the model alloys, as shown in Figure 2-2, it can be concluded that the highest average filament lengths are obtained for the Al-Cu binary alloys. The other model alloys are far less susceptible to filiform corrosion propagation with average filament lengths all smaller than 1.32 mm, compared to 2.84 and 7.78 mm for the degreased Al-0.20Cu and Al-1.00Cu alloys respectively.

![Figure 2-2: Average filament length after 1000 hours of accelerated filiform corrosion test exposure for three pretreatments. The alloy codes are listed in Table 2-1.]

The trend of an increasing average filament length with the alloying concentration is especially clear for the highly susceptible Al-Cu binary alloys and also for the degreased Al-Si alloys. This in contrast with the degreased Al-Zn and Al-Mg alloys which show no or little significant increase in average filament length with solute content. Generally, chromating also proves to be very effective in reducing the filiform corrosion propagation properties of the tested substrates. Besides the highly susceptible Al-Cu alloys, the Al-3.06Mg and the technical alloys, all other model alloys had no or only filaments smaller
than 0.5 mm after chromating. For the chromated binary alloys the average filament length was too low to determine a relation between the alloying concentration and the filiform corrosion propagation. After cerating, the model and technical alloys still show significant filiform corrosion propagation, i.e. average filament lengths ≥0.5 mm, with the exception of the Al-0.44Mg alloy. No clear relation between the alloying concentration and filiform corrosion propagation can be determined for the cerated binary alloys, except for the highly susceptible Al-Cu binary alloys. Although the average filament lengths for the degreased AA2024-T351 and AA7075-T651 alloys presented in Figure 2-2 are only qualitative indications, a higher front corrosion length can be observed for the degreased AA2024-T351 compared to the degreased AA7075-T651. A decrease in average filament length, i.e. front corrosion length for the degreased samples, can be observed after chromating or cerating of the AA2024-T351 alloy.

2.3.3 Corrosion number

Figure 2-3 indicates large differences in the corrosion number between the various alloy systems and surface pretreatments.

A maximum corrosion number of ~16 was obtained for the Al-1.00Cu alloy, whereas for the cerated Al-0.44Mg alloy no filiform corrosion attack was found after the 1000 hours accelerated filiform corrosion test.

When evaluating the corrosion number data of the binary alloy system it is evident that the average corrosion number decreases in the order Al-Cu, Al-Si, Al-Zn, Al-Mg. A further observation is that per binary alloy system the corrosion number increases with the alloying concentration which is in line with observations presented in the literature [2.24,2.25]. This trend is particularly clear for the degreased samples. On the chromated and cerated samples the filiform corrosion attack was too small to confirm such a relation with any statistical significance, but the data would not contradict such a conclusion. The detrimental effect of Cu as an alloying element in aluminium is very obvious for this set of experiments. The degreased AA2024-T351 show significantly more filiform corrosion attack compared to the AA7075-T651 alloy, with indicative corrosion numbers of 7.62 and 1.42 respectively.

The chromate conversion coating results in a slightly lower corrosion number for the AA2024-T351, compared to the AA7075-T651, whereas the cerate conversion coating results in a slightly lower corrosion number for the AA7075-T651, compared to the AA2024-T351. Generally, the corrosion number for the chromated and cerated technical
alloys only vary from 2.16 for the cerated AA7075-T651 to 2.78 for the cerated AA2024-T351.

**Figure 2-3:** Corrosion number after 1000 hours of accelerated filiform corrosion test exposure for three pretreatments. The alloy codes are listed in Table 2-1.

### 2.4 Conclusions

The accelerated filiform corrosion exposure tests show both a compositional and a pretreatment effect on the filiform corrosion behaviour of the tested substrates. For all tested degreased binary alloys, the site density increases with increasing concentration of the alloying element. The trend of an increasing average filament length with the alloying concentration is especially clear for the highly susceptible Al-Cu binary alloys and also for the degreased Al-Si alloys. This is in contrast with the degreased Al-Zn and Al-Mg alloys which show no or little significant increase in average filament length with solute content. Evaluation of the total filiform corrosion attack, defined as the product of the site density and the average filament length, shows that the average corrosion number decreases in the
order Al-Cu, Al-Si, Al-Zn, Al-Mg. A further observation of the corrosion number data of the binary alloy system is that the corrosion number increases for all binary alloys with the alloying concentration. These observations support the applicability of the fundamental cause of local corrosion processes to filiform corrosion on aluminium alloys. Successive interactions between the alloy matrix and particles are likely to be affected by the alloying elements and their concentrations. The trend of an increasing corrosion number with alloying concentration is particularly clear for the degreased samples. On the chromated and cerated samples the filiform corrosion attack was too small to confirm such a relation with any statistical significance, but the data would not contradict such a conclusion.

REFERENCES

2.6 Z. SZKLARASKA-SMIALOWSKA, *Corrosion* 27 (1971) p. 223
2.9 G.S. CHEN, M. GAO and R.P. WEI, *Corrosion* 52 (1996) p. 8
2.11 K. NISANCIOGLU, H. LETH-OLSEN and O. LUNDER, Corrosion protection by
Chapter 2


2.13 H.A. KATZMAN and G.M. MALOUFF, Appl. of Surface Sci. 2 (1979) p. 416

2.14 D.J. McCOY, Proceedings 2nd AESF/EPA Chromium Colloquium Miami, FL, February 1990


2.23 Deutsches Institut Für Normung e.V., Number 65472: Filiform corrosion test of coatings on aluminium alloys, draft (1989)


A potentiodynamic polarisation study on some binary aluminium alloys and its relation to filiform corrosion

The aim of the present investigation is a combined study of filiform corrosion of Al-Cu and Al-Zn binary aluminium alloys by accelerated exposure tests, as presented in Chapter 2, and potentiodynamic polarisation measurements.

3.1 Introduction

The accelerated exposure tests of the binary aluminium alloys as presented in Chapter 2 have shown a trend of a higher filiform corrosion susceptibility with increasing alloying element concentrations for all model systems. Furthermore, the filiform corrosion susceptibility varies with the solute atom. In particular Cu was found to have a detrimental effect on the filiform corrosion properties.

While the detailed examination of the filiform corrosion rate as a function of the substrate composition and the surface pretreatment applied yields valuable results, it does not
provide explanations for observed dependencies. The underlying mechanisms for filiform corrosion can only be further elucidated by performing electrochemical measurements in media characteristic for the corrosion process studied. To this aim potentiodynamic polarisation measurements in synthetic anolyte and catholyte media, which are characteristic for the local anodic and cathodic sites in the filaments on the aluminium substrates, are performed on six of the most interesting alloys.

3.2 Theoretical background

Potentiodynamic polarisation measurements are performed in bulk anolyte and catholyte solutions which are characteristic for local anodic and cathodic sites in filaments on aluminium substrates, resulting from the differential aeration and subsequent anodic undermining [3.1,3.2], as presented in Figure 1-6. The differential aeration results in spatial separation of the anodic site in the active tip of the filament, where aluminium dissolves, and the cathodic site at the passive trailing area, where oxygen is reduced to produce hydroxyl ions. The anodic and cathodic sites are spatially separated by a poorly defined membrane, similar to the membrane of solid corrosion products reported by Van der Weijde et al. [3.3] for cathodic delamination on iron based substrates. Recently, it is also suggested that the cathodic site is located at the front of the area where corrosion products are deposited [3.4]. Chloride ions are essential to provide electrolyte conductivity and to stimulate the initiation of corrosion and these ions migrate with the filament head and are only partially incorporated in the hydrated corrosion products in the filament tail.

Initial investigations on extruded AA1050 alloys with the use of a macro differential aeration cell by Lobry et al. [3.5], mainly focusing on the effect of variations of electrolyte pH and chloride concentrations, confirm the differential aeration principle for filiform corrosion on aluminium.

The theoretical background of the combined study of accelerated exposure tests and potentiodynamic polarisation measurements is briefly discussed here. A more detailed and fundamental correlation is presented by Huisert et al. [3.6].

The anodic dissolution reaction of aluminium in the presence of chloride ions is [3.7]:

\[
\text{Al} + 2 \text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Al(OH)}_2\text{Cl} + 2 \text{H}^+ + 3 \text{e}^- \quad (3-1)
\]
Due to the acidity at the anodic site also hydrogen evolution takes place as a secondary cathodic reaction:

\[ 2\ H^+ + 2\ e^- \rightarrow H_2 \ (g) \]  \hspace{2cm} (3-2)

Also in this work the evolution of gas bubbles in the filament tip has been observed. In line with the literature [3.8,3.9] and Equation (3-2) these bubbles are taken to be hydrogen bubbles. The main cathodic reaction at the cathodic site will be the reduction of oxygen:

\[ O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^- \]  \hspace{2cm} (3-3)

The number of electrons produced by the anodic dissolution should be equal to the number of electrons consumed by the cathodic reactions. The net production of electrons at the anodic site, i.e. resulting from the aluminium dissolution and hydrogen reduction reactions, is consumed at the spatially separated cathodic site. This electronic current is equal to the net ionic current through the electrolytes and in this paper defined as the filiform corrosion current.

Following the basic principles of the mixed-potential theory [3.10], this filiform corrosion current can be derived from the potentiodynamic polarisation measurements by determination of the intercept of the anodic part of the polarisation curve in the anolyte and the cathodic part of the polarisation curve in the catholyte, assuming a certain effective cathode/anode area ratio. The electrolyte resistance between the anodic and cathodic sites in real filaments is therefore not taken into account in the potentiodynamic polarisation measurements. In the present investigation this filiform corrosion current is related to the filiform corrosion properties during the accelerated exposure tests. A relatively high filiform corrosion current implies a relatively high number of electrons produced at the anodic site as a result of the anodic aluminium dissolution reaction, according to Equation (3-1). The local morphology of corrosion attack within the filament may vary with alloy composition and pretreatment. During the present investigation the filiform corrosion current is related to one-dimensional propagation properties of the filaments. Filament width and in-depth attack are considered to be similar and constant for comparable systems. Consequently, according to this theory, a relatively high filiform corrosion current should correlate with a higher filiform growth rate.
As the exact anolyte and catholyte compositions are still unknown, the following considerations have been used as a basis for the formulation of electrolytes for potentiodynamic polarisation measurements. Slabaugh [3.8] and Hoch [3.11] have reported the acidity in the filament tip to be at a pH of 1 to 2. During the present investigation these low pH values are confirmed by opening a filament by scalpel using around a filament through the organic coating, lifting the coating, immediately followed by testing the electrolyte in the filament tip by narrow range pH indicator paper: these results are presented in Chapter 4. Slabaugh [3.8] also reported the presence of chlorides in the filament tip and also during the present investigation qualitative SEM/EDX analysis of filaments gave evidence of high chloride concentrations at the very tips of filaments. Due to the anodic dissolution of aluminium, also aluminium ions should be present. Finally, according to the differential aeration theory [3.1,3.2], the oxygen concentration at the anodic site is expected to be very low, as the oxygen diffuses mainly through the tail of the filament and is reduced just behind the anodic site. The catholyte is assumed to be alkaline as a result of the reduction of oxygen at the cathodic site. Both the exact value of the pH of the catholyte and the effective cathode/anode area ratio are hard to determine in practice because of the low liquidity just behind the tip.

### 3.3 Experimental

In this section the base material details, the choice of electrolytes and the electrochemical set-up are discussed.

#### 3.3.1 Base material

The combined filiform corrosion and electrochemical study is validated by analysing both highly and less filiform corrosion susceptible substrates. For these reasons both the two Al-Cu and the four Al-Zn model alloys are studied both on their filiform corrosion properties and their potentiodynamic polarisation response. The composition and alloy codes are listed in Table 3-1. Only degreased samples are analysed during the present combined study to ensure that the compositional variations in the substrates are the only variables to dedicate the variations in the potentiodynamic polarisation response.
The alloys have been DC cast as 20x7.5 cm blocks on a 99.998% base, scalped, homogenised 16h at 465 °C, hot-rolled to 15-20 mm, reheated 1h at 465 °C, hot rolled to 6 mm, cold-rolled to 4 mm, solution heat treated at 550/650 °C followed by a cold water quench, cold rolled to 1.1-1.2 mm and flattened in a hot press at 225 °C pressing plate temperature for 12 mins.

Prior to the potentiodynamic polarisation measurements, all alloys are carefully cleaned with ethanol and subsequently immersed for 10 minutes in Brulin Formula 815 GD (alkaline cleaner) at 60°C, followed by a cold water rinse in running tap water for 5 minutes.

Table 3-1: Composition and alloy code of binary and ternary model alloys

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Alloying concentration [wt-%]</th>
<th>Alloy code</th>
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<tbody>
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<td>Al-1.00Cu</td>
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</tr>
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</table>

3.3.2 Choice of electrolytes

As discussed in section 3.2 and in the publication of Huisert et al. [3.6], the exact anolyte and catholyte compositions have not been reported in the literature yet. However, in the literature pH values of 1-2 [3.8,3.11] and high chloride concentrations [3.8] in the very filament tips are reported, which are confirmed during the present investigation. Furthermore, due to the anodic dissolution of aluminium, aluminium ions should be present at the anodic site and following the differential aeration theory [3.1,3.2], the oxygen concentration at the anodic site is expected to be very low. Following these considerations the potentiodynamic polarisation measurements typical for the anodic site are performed in the following anolyte: 0.86 M NaCl + 0.1 M AlCl₃, acidified to pH 2 with concentrated HCl (33%) and actively deaerated with high purity nitrogen gas. The catholyte is assumed to be alkaline as a result of the reduction of oxygen and water at the cathodic site, as presented in Equation (3-3). Assuming total
electroneutrality and an effective cathode/anode area ratio of 100, the polarisation measurements in the catholyte are conducted in a solution of distilled water adjusted to pH 10 by addition of NaOH and actively aerated with air, to ensure a constant and fixed oxygen concentration during the potentiodynamic polarisation measurements.

3.3.3 Electrochemical set-up and potentiodynamic polarisation procedure

The electrochemical cell consisted of an Avesta cell [3.12], the aluminium based alloy as a working electrode (working area 0.8 cm²), a commercial saturated calomel reference electrode (SCE) and a platinum cylindrical small-mesh wire netting counter electrode. Prior to the electrochemical measurements the specimens are degreased with ethanol and Brulin 815 GD. The open circuit potential (OCP) of the system was allowed to become stationary over a 5 hour period before the commencement of the polarisation scans. Even though some corrosion did occur during this period, the time at the OCP prior to testing did ensure that the system was stable, enabling proper potentiodynamic polarisation measurements at a stable OCP on a surface representative of an active anodic or cathodic site in a filament. The scan rate for the potentiodynamic polarisation experiments was 0.2 mV/sec and were started at cathodic potentials. The scans in the anolyte were started at −100 mV vs. OCP to +200 mV vs. OCP; in the catholyte the scans were started at −200 mV vs. OCP to +100 mV vs. OCP. The potentiodynamic polarisation scans were carried out at room temperature using a PAR273A potentiostat.

3.4 Results and discussion

For all Al-Cu and Al-Zn binary aluminium alloys the values of the site density, average filament lengths and corrosion numbers after 1000 hours of accelerated exposure are presented in Chapter 2. The Al-Cu alloys showed increasing filiform corrosion initiation and propagation characteristics with increasing Cu concentration, while the Al-Zn alloys showed increasing site density with Zn concentration, but no significant increase in average filament length.
3.4.1 Potentiodynamic polarisation measurements

For the degreased Al-Cu and Al-Zn binary alloys the characteristic potentiodynamic polarisation scans in both the anolyte and the catholyte are shown in Figure 3-1(a) and 3-1(b) respectively.

**Figure 3-1:** Typical potentiodynamic polarisation measurements for the Al-Cu (a) and the Al-Zn (b) binary alloys in the anolyte and catholyte solutions. The vertical dashed arrows indicate the filiform corrosion current value for each alloy. (effective cathode/anode surface area assumed to be 100)
The characteristic potentials and the filiform corrosion currents derived from the potentiodynamic polarisation measurements are listed in Table 3-2. A higher OCP for the Al-1.00Cu alloy both in the anolyte and in the catholyte compared with the Al-0.20Cu alloy is clear. The OCPs for the Al-0.20Cu and Al-1.00Cu alloys in the catholyte are respectively -0.77V vs. SCE and -0.64V vs. SCE. The pitting potential (-0.73 V vs. SCE) and the OCP (-0.75 V vs. SCE) for the Al-1.00Cu binary alloy in the anolyte appear to be very close.

For the Al-0.20Cu binary alloy in the anolyte the pitting potential and the OCP appear to be more distinct and to be at values of respectively -0.74V vs SCE and -0.80V vs SCE. The difference between the OCPs of the Al-1.00Cu in the anolyte and catholyte is higher than the OCP of the Al-0.20Cu in both electrolytes: respectively about 0.11V and 0.03V. Another important observation is that the Al-Cu alloys show an increase of the cathodic current in both the anolyte and the catholyte with increasing Cu concentration.

**Table 3-2:** Summary of the characteristic potential and filiform corrosion current values for the Al-Cu and Al-Zn model alloys under anolyte and catholyte conditions

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Open Circuit Potential vs. SCE [V]</th>
<th>Pitting Potential vs. SCE [V]</th>
<th>Passive range [V]</th>
<th>Filiform Corrosion Current [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anolyte</td>
<td>Catholyte</td>
<td>Anolyte</td>
<td>Catholyte</td>
</tr>
<tr>
<td>Al-0.20Cu</td>
<td>-0.80</td>
<td>-0.77</td>
<td>-0.74</td>
<td>0.06</td>
</tr>
<tr>
<td>Al-1.00Cu</td>
<td>-0.75</td>
<td>-0.64</td>
<td>-0.73</td>
<td>0.02</td>
</tr>
<tr>
<td>Al-0.19Zn</td>
<td>-0.93</td>
<td>-0.87</td>
<td>-0.80</td>
<td>0.13</td>
</tr>
<tr>
<td>Al-0.48Zn</td>
<td>-0.92</td>
<td>-0.77</td>
<td>-0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>Al-0.97Zn</td>
<td>-0.96</td>
<td>-0.78</td>
<td>-0.90</td>
<td>0.06</td>
</tr>
<tr>
<td>Al-2.09Zn</td>
<td>-0.97</td>
<td>-0.84</td>
<td>-0.97</td>
<td>0.00</td>
</tr>
</tbody>
</table>

For the degreased Al-Zn binary alloys the characteristic scans in both the anolyte and the catholyte are shown in Figure 3-1(b). The OCP values in the catholyte for the Al-Zn alloys show an increase from Al-0.19Zn to Al-0.48Zn, which is followed by a small drop in OCP from Al-0.48Zn to Al-0.97Zn and Al-2.09Zn. The OCP values in the anolyte show an overall small decrease of OCP with increasing Zn concentration. In contrast, the pitting
potentials of these Al-Zn alloys in the anolyte show large variations and decrease strongly with increasing Zn concentration. For the Al-0.19Zn the difference between the pitting potential and the OCP is the largest and this difference decreases with increasing Zn concentration: for the Al-2.09Zn alloy the pitting potential coincides with the OCP.

Another important observation is the decrease of cathodic current in the anolyte, resulting from the hydrogen reduction reaction, with increasing alloying concentration, unlike the observations on the Al-Cu alloys. The cathodic current in the catholyte only shows an initial increase in cathodic current from the Al-0.19Zn to the Al-0.48Zn sample but a further increase in Zn concentration yields little additional changes in the cathodic current in the catholyte. Furthermore, Figures 3-1(a) and 3-1(b) show that if the cathode surface area is taken equal to the anode area (i.e. the catholyte curve shifts two orders of magnitude to the left because of the current surface area ratio of 100), the electrical current in the catholyte is always much lower than that in the anolyte at the same potential. This mainly originates from the availability of hydrogen ions in the anolyte.

3.4.2 Theoretical determination of the filiform corrosion current

The filiform corrosion current can be approximately calculated using Equation 3-4, and with the measured filiform corrosion current a theoretical anode/cathode area ratio can be calculated:

\[
\text{Filiform corrosion current} = \frac{w \cdot t \cdot v \cdot \rho \cdot n \cdot F}{M} \quad (3-4)
\]

With:

- \( w = \) filament width [m] ; \( w = 5 \cdot 10^{-4} \)
- \( t = \) average depth of attack [m] ; \( t = 1 \cdot 10^{-7} - 2 \cdot 10^{-6} \)
- \( v = \) filament propagation rate [m/s] ; \( v = 2.2 \cdot 10^{-9} \)
- \( \rho = \) density [g/m³] ; \( \rho = 2.7 \cdot 10^{6} \)
- \( n = \) number of electrons per dissolving atom[] ; \( n = 3 \)
- \( F = \) Faraday's constant [C/mol] ; \( F = 9.65 \cdot 10^{4} \)
- \( M = \) Molar mass [g/mol] ; \( M = 27 \)

\( \rho, n, F, M \) are fixed values assuming the dissolution of aluminium atoms only during filiform corrosion. The parameter values used are general or those determined for the Al-
1.00Cu degreased only sample. The filament propagation rate is assumed to be constant during the accelerated exposure time of 1000 hours and was therefore determined to be $2.2\times10^{-9}$ m/s. The filament width for these samples was measured to be $5\times10^{-4}$ m and the average depth of attack was measured by confocal laser microscopy as shown in Figure 3-2, and determined to vary between about $1\times10^{-7}$ and $2\times10^{-6}$ m.

![Figure 3-2](image)

**Figure 3-2:** Confocal laser microscopy of the typical filiform corrosion attack morphology (a) on an Al-1.00Cu degreased only sample showing an approximate average depth of attack of $\sim 2 \, \mu m$ (b)

With these values the filiform corrosion current in the filament is calculated to be $3.18\times10^{-9}$ – $6.37\times10^{-8}$ A. Estimating the anodic area of the filament to be about $1\times10^{-7}$ m$^2$ and with the
working area of the Avesta cell of $8 \times 10^{-5} \text{ m}^2$ the theoretical filiform corrosion current to be measured with the Avesta cell should vary between $2.55 \times 10^{-6} \text{ A}$ and $5.10 \times 10^{-5} \text{ A}$. The measured value of $2.00 \times 10^{-5} \text{ A}$, as shown in Table 3-2, lies within this theoretical range. The value of $2.00 \times 10^{-5} \text{ A}$ was based on the assumption that the effective cathode/anode ratio was 100. The theoretical cathode/anode area ratio would be $12.7 - 254.8$, assuming an anode area of $1 \times 10^{-7} \text{ m}^2$.

3.4.3 Combination of potentiodynamic polarisation and filiform corrosion results

With the analysis of the filiform corrosion current as presented in this chapter one has to keep in mind that the filiform corrosion current in real filaments could differ significantly from the presented values, depending on the actual anodic and cathodic areas and the effective cathode/anode area ratio in real filaments. However, assuming a fixed effective cathode/anode area ratio for the alloys investigated, the correlation between the filiform corrosion current and the filiform corrosion properties would still apply. Furthermore, the present analysis does not take into account the electrolyte resistance between the anodic and cathodic sites in real filaments. Lobry et al. [3.5] have shown for their system that the potential difference between anode and cathode of a macro differential aeration cell with an electrolytical connection is very small (~10-20 mV) and very close to the OCP of the anode before the connection. This supports our present observations and incorporation of an electrolyte resistance into the model would not affect the correlation between the filiform corrosion current and the filiform corrosion properties. The correlation between the filiform corrosion characteristics and filiform corrosion current is presented in Figures 3-3 and 3-4 for the degreased Al-Cu and Al-Zn binary alloys. The filiform corrosion currents and relevant potentials are also summarised in Table 3-2. It has to be noted that in the present analysis the filiform corrosion current is related to one-dimensional propagation rates of the filaments when filament width and in-depth attack are considered to be constant for comparable systems. Figure 3-3 clearly shows that for the Al-Cu binary alloys a higher filiform corrosion current corresponds with a significantly higher average filament length after 1000 hours of accelerated exposure. This higher filiform corrosion current also corresponds with an increasing Cu concentration in the alloy. These observations are in line with the investigation of Huisert et al. [3.6], who have reported an increasing filiform corrosion current with increasing average filament length for AA3000 series alloys. Although the samples and corresponding measurements
can not be related directly, the corrosion currents found by Huisert et al. [3.6] are of the same order of magnitude as our filiform corrosion currents and in the range of $10^{-6}$-$10^{-5}$ A, assuming an effective cathode/anode area ratio of 100. Also the corresponding average filament lengths after 1000 hours of accelerated exposure test are similar and in the order of 1-10 mm.

![Graph showing corrosion currents and filament lengths for Al-Cu and Al-Zn alloys](image)

**Figure 3-3:** The correlation between the filiform corrosion current and the average filament length for the degreased Al-Cu binary alloys and the Al-Zn binary alloys.

Such a relation of a higher filiform corrosion current corresponding with a higher average filament length is less clear for the less filiform corrosion susceptible Al-Zn binary alloys. The increasing filiform corrosion current is hardly reflected in an increasing average filament length for these alloys. The average lengths after 1000 hours of accelerated exposure test only vary from 1.14 to 1.25 mm, whereas the filiform corrosion currents vary from $4.7\cdot 10^{-6}$ to $3.9\cdot 10^{-5}$ A. Figure 3-4 shows a very clear increase of the corrosion number with increasing filiform corrosion current and corresponding alloying concentration for the Al-Cu alloys. Although for the Al-Zn alloys a small absolute increase in corrosion number, 0.32 for the Al-0.19Zn to 0.60 for the Al-2.09Zn, with increasing filiform corrosion current
is observed, the relative increase is deemed significant. As the average filament length is more or less constant for the Al-Zn alloys, the increase in corrosion number mainly reflects an increase in the filament site density. The clear increase in the filiform corrosion current mainly results from the changes in the anodic curves in the anolyte, i.e. while the cathodic curves in the catholyte do not show large differences (besides the initial increase from Al-0.19Zn to Al-0.48Zn), the pitting potential and the passive range decrease with Zn concentration as shown in Figure 3-1(b) and Table 3-2.

![Filiform corrosion current graph](image)

**Figure 3-4:** The correlation between the filiform corrosion current and the corrosion number for the degreased Al-Cu binary alloys and the Al-Zn binary alloys.

Further analysis of Figures 3-3 and 3-4 shows that the higher average filament length and corrosion number for the Al-Cu alloys compared to those for the Al-Zn alloys with similar alloying concentrations are not reflected in a higher filiform corrosion current. When comparing the results for the Al-Cu and Al-Zn binary alloys it can be concluded that the correlation differs significantly with the solute atom and the filiform corrosion current turns out to be a non-uniquely discriminating parameter for the filiform corrosion susceptibility of the set of model alloys investigated. However, the observed relative filiform corrosion behaviour on Al-Cu and Al-Zn alloys can be rationalised by a more
detailed analysis of the information in the potentiodynamic diagram shown schematically in Figure 3-5 for a set of alloys. ‘A’ indicates the position of the filiform corrosion current defined as the intercept of the cathodic curve in the catholyte and the anodic curve in the anolyte, as discussed in detail in the theoretical background section. Curve ‘B’ indicates an increasing hydrogen reduction reaction rate in the anolyte and implicitly a higher sensitivity to local variations of substrate composition: these local variations can significantly influence the local potential values and herewith the local corrosion reaction rates. The length of vector ‘C’ indicates the passive range under anolyte conditions which we relate to the filiform corrosion initiation characteristics: a smaller passive range corresponds to more rapid pitting and hence to a higher number of filiform corrosion initiations per scratch length, in this chapter defined as the site density parameter.

Figure 3-5: Schematic representation of the potentiodynamic polarisation curves in the anolyte and catholyte solutions.

We can now re-examine the electrochemical information in Figure 3-1 and Table 3-2. For the Al-Cu alloys the cathodic current in both the anolyte and the catholyte increases with the Cu concentration. This higher cathodic current, with an accompanying higher anodic dissolution rate, leads to a higher propagation rate, in line with the average filament length data. However, for the Al-Zn alloys an overall decrease of the cathodic current in the anolyte with increasing Zn concentration was observed in combination with a rather
constant cathodic current in the catholyte. For this reason the filiform corrosion propagation rate is not likely to increase with increasing Zn concentration, which is again in line with the average filament length data from the present investigation, showing no significant differences in average filament lengths for the Al-Zn model alloys.

For the Al-1.00Cu alloy the pitting potential was very close to the OCP, whereas the Al-0.20Cu showed a more distinct difference between the pitting potential and the OCP. If the ease of filiform corrosion initiation is related to the ease of pitting for a specific alloy, this would explain the higher site density for Al-1.00Cu compared to that for the Al-0.20Cu. The site density as a function of the passive range for both the Al-Cu and Al-Zn alloys is presented in Figure 3-6.

![Figure 3-6](image)

**Figure 3-6:** The site density for the degreased Al-Cu and Al-Zn model alloys as a function of the passive range in the anolyte.

The increased ease of pitting will also enhance the propagation rate. The supposed correlation between ease of pitting and the ease of filiform corrosion initiation is also clear for the Al-Zn alloys. The reduction in passive range with increasing Zn concentration, corresponds to an increase of the site density, as presented in Figure 3-6. This potentially easier pitting behaviour with increasing Zn concentration is not reflected in a higher
propagation rate because of the opposing trends in cathodic current changes both in the catholyte and anolyte as a function of Zn concentration discussed above.

3.5 Conclusions

The accelerated filiform corrosion exposure tests presented in Chapter 2 show a clear compositional effect on the filiform corrosion behaviour of the tested substrates. For all tested degreased Al-Cu and Al-Zn binary alloys, the site density increases with increasing concentration of the alloying element. The trend of an increasing average filament length with the alloying concentration is especially clear for the highly susceptible Al-Cu binary alloys. This is in contrast with the degreased Al-Zn alloys, which show no or little significant increase in average filament length with Zn concentration. Evaluation of the total filiform corrosion attack, defined as the product of the site density and the average filament length, has shown that the corrosion number increases for all Al-Cu and Al-Zn alloys with the alloying concentration.

The results of the present set of experiments are in line with preceding investigations and a correlation between the polarisation measurements and both filiform corrosion propagation and total attack after the accelerated exposure test for the Al-Cu binary alloys is observed. Such a correlation is not observed for the Al-Zn alloys as an increasing filiform corrosion current is barely reflected in a higher average filament length. When comparing the results for the Al-Cu and Al-Zn binary alloys it can be concluded that the correlation differs significantly with the solute atom and the filiform corrosion current as defined turns out to be a non-uniqely discriminating parameter for the filiform corrosion susceptibility of the set of model alloys investigated in the present research. The different correlations for the Al-Cu and Al-Zn alloys are explained from the electrochemical response to local variations of the substrate composition. These local compositional variations will result in a higher overall cathodic and anodic reaction rate with increasing Cu concentration for the Al-Cu alloys. For the Al-Zn alloys a more constant overall cathodic and anodic reaction rate as a function of the Zn concentration is observed. This explains the increasing average filament length with Cu concentration and more constant average filament length with increasing Zn concentration after 1000 hours of accelerated exposure testing.

For the Al-Cu and Al-Zn model alloys the filiform corrosion initiation characteristics are related to the passive range and thus implicitly to the ease of pitting of the alloy. A smaller
passive range results in higher filiform site density for both the Al-Cu and Al-Zn alloys.

References

3.2 H. KAESCHE, Werkstoffe und Korrosion 11 (1959) p.668
3.8 W.H. SLABAUGH, W. DEJAGER, S.E. HOOVER and L.L. HUTCHINSON, J. of Paint Techn. 44 (1972) p. 76
In this chapter a mechanistic study into filiform corrosion on AA2024-T351 is presented. To this aim several physical and chemical characterisation techniques on a macro- and microscopic scale were exerted to further elucidate the general and local mechanism of filiform corrosion on aluminium. These techniques include Kelvin Probe measurements, pH measurements in the local solute at the filament tip, time lapse video recording of phenomena, such as hydrogen evolution, in the filament tip and SEM/EDX analysis of the filiform corrosion attack.

4.1 Introduction

In Chapter 1 of this thesis, an overview is given of the present insights into the parameters that play an important role in the filiform corrosion process on aluminium alloys. It is shown that filiform corrosion is a complex phenomenon, involving contributions from the environment, the organic coating, the coating-substrate interface and the microstructure of the substrate (surface). Microstructural variations in the substrate influence the general and local electrochemical characteristics of the alloy and also the quality of the overlying oxide
layer. For these reasons it can be argued that the microstructure of aluminium alloys plays an important role in the filiform corrosion susceptibility of aluminium alloys. While the detailed examination of the filiform corrosion rate in relation to the substrate composition, i.e. type of alloying elements and their concentration, and the surface pretreatment applied as presented in Chapter 2 yields valuable results, it does not provide explanations for the observed dependencies. Therefore, in addition to the electrochemical measurements presented in Chapter 3, a search for more detailed mechanistic understanding of the filiform corrosion process in general and the role of microstructural heterogeneities in aluminium alloys is of scientific interest and technological importance. To this aim several physical and chemical analysis techniques were used to further elucidate the filiform corrosion process on the typical aircraft aluminium alloy AA2024-T351. First, a short overview of the techniques used and background of the experiments will be discussed.

4.1.1 Scanning Kelvin Probe (SKP)

A relatively novel characterisation technique, introduced to the field of corrosion research by Stratmann et al. [4.1-4.3], is the Scanning Kelvin Probe (SKP) technique. A brief theoretical background of the SKP measurements is presented now. Under atmospheric conditions, thin electrolyte layers are formed on top of metal surfaces by adsorption or condensation. With the SKP technique, the Volta potential difference between the electrolyte and the metal is measured with an oscillating electrode, the so called Kelvin probe, without disturbing the composition or electrochemical properties of the electrolyte layer and metal under investigation. The oscillating probe and the sample can be seen as a capacitor when electronically connected. The oscillations of the probe cause a variation in the capacitance across the air gap, thereby introducing an alternating current in the circuit. The magnitude of this alternating current depends on the Volta potential difference. From the measured Volta potential difference, the corrosion potential can be derived mathematically. The Volta potential has been shown to vary linearly with the corrosion potential of the sample/solution interface. Further details of these derivations and the theoretical background of the SKP are extensively discussed by Stratmann et al. [4.1-4.4]. The main advantage of the SKP measurement in coating research lies in the fact that theoretically the presence of a non-conducting polymer coating between the vibrating probe and the electrolyte covered metal, should not influence the measurement. Measurement of
the corrosion potential under an organic coating provides information on defects at the metal-coating interface. Many investigations have been focussed so far on underfilm corrosion [4.5-4.11]. During the present research the SKP technique is used to detect local anodic and cathodic sites in filaments on AA2024-T351 in order to confirm the anodic undermining mechanism for filiform corrosion on aluminium alloys, as presented in Chapter 1.

4.1.2 pH measurements and time lapse video analysis

Slabaugh et al. [4.12] examined the acidity generated in filaments in more detail. The most effective procedure found for measuring the pH of the filiform tip was to open the filament and immediately test the fluid with slightly moistened narrow range pH indicator paper. This consistently gave pH values of 1.5 to 2.0. In view of the dilution effect by the moisture in the pH indicator paper, the pH was estimated to be near a value of 1. A series of specific indicators such as methyl violet, methyl green and methacresol purple, incorporated into the organic coating or applied at the coating-substrate interface gave similar results. Tiny bubbles, taken to be hydrogen bubbles, were reported to evolve from the leading edges of the corrosion part. These bubbles flowed back from the edge and collected into larger bubbles toward the rear of the fluid in the filament tip.

Hoch et al. [4.13, 4.14] have studied the acidity in filaments by incorporation of wide range pH indicators into moisture permeable primers and application of a clear polyurethane top coating. The active filament heads developed extremely acid pH (in the vicinity of 1.0) and hydrogen gas evolution was again observed in the anolyte. In literature [4.12-4.15] gas evolution is often observed in the tip of the filament head and as no chemical analysis of these bubbles is reported, these bubbles are taken to be hydrogen bubbles.

During the present investigation the pH values in the filament tips on AA2024-T351 were studied and also the gas evolution and transport of species in filament heads were analysed in more detail.

4.1.3 Scanning Electron Microscopy / Energy Dispersive X-ray analysis (SEM/EDX)

As presented in Chapter 1, the chloride containing acidic anolyte provides the necessary condition for chemical breakdown of the protective coating-substrate interface (i.e. natural oxide or pretreatment layer), exposing the substrate microstructure. This process includes the
chloride release from transitory aluminium hydroxychloride complexes providing
electron-neutrality conditions in the anolyte and continuous participation of a more or less
constant number of chloride ions in the substrate surface attack. However, some entrapment
of chloride in the corrosion product filled filament tail is reported in the literature which
could result in a stagnation of filament growth rate after considerable exposure times [4.12,
4.15-4.17], in addition to the effect of a decrease of oxygen concentration gradient with
increasing filament lengths [4.17-4.19].
Detection of chloride ions in filaments and local filiform corrosion attack on AA2024-
T351 is performed by SEM/EDX.

4.2 Experimental

Commercial AA2024-T351 alloys were used as the base material for all filiform corrosion
tests and subjected to a range of experimental techniques to further elucidate the general and
local filiform corrosion process on aluminium alloys. In this section, the experimental details
of the material and the analysis techniques are presented.

4.2.1 Preparation of the samples

The chemical composition of two sets of commercial AA2024-T351 is presented in Table 4-
1.
The first set of AA2024-T351 samples (L x LT x T = 67 x 60 x 1.2 mm) was used as a base
material for Scanning Kelvin Probe analysis. The second set of AA2024-T351 samples (L x
LT x T = 76 x 128 x 1.6 mm) was used for the pH measurements, video analysis, corrosion
attack and chemical analysis. This second set of samples is the same set of panels as
analysed for their filiform corrosion initiation and propagation characteristics which were
presented in Chapter 2.
The first set of samples (AA2024-T351-I) was pretreated, according to the following
procedure:

- Degreasing by immersion in AD Chemicals Cleaner Z19 (weak phosphoric acid based
  commercial degreasing agent) during 20 seconds at 56 °C, followed by a cold tap water
  rinse (the ‘water-break-free surface’ was checked to ensure complete removal of grease)
Mechanistic investigation into filiform corrosion on AA2024-T351

- Application of a chromate-phosphate conversion coating by immersion in AD Chemicals Unicon 87 during 20 seconds at 43 °C, followed by rubber rolling the sample surface to homogenise the conversion coating
- Drying the samples at a peak material temperature of 150 °C during 15 seconds

Following the pretreatment, a clear polyester coating was applied with a wire bar and cured at a peak material temperature during 55 seconds at 240 °C. The mean dry coating thickness in this case is ~20 μm. The reverse side of the panels is protected by an air-drying polyester coating with a layer thickness of ~21 μm.

**Table 4-1: Chemical composition of the two sets of AA2024-T351 as determined by XRF [wt-%]**

<table>
<thead>
<tr>
<th>Element</th>
<th>AA2024-T351-I</th>
<th>AA2024-T351-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.51</td>
<td>4.39</td>
</tr>
<tr>
<td>Mg</td>
<td>2.28</td>
<td>1.29</td>
</tr>
<tr>
<td>Mn</td>
<td>0.66</td>
<td>0.67</td>
</tr>
<tr>
<td>Fe</td>
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<td>0.07</td>
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<td>0.15</td>
</tr>
<tr>
<td>Al</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

Three pretreatments are imposed on the second set of samples (AA2024-T351-II). The application procedures of these three pretreatments, degreasing only, chromating and cerating are described in detail in Chapter 2, section 2.2.2. Following the pretreatment, an air-drying clear flexible polyurethane coating was spray deposited in two stages with a mean dry coating thickness of 42 μm in total (standard deviation 4 μm). The coating defect was applied by scribing perpendicular to the rolling direction with a scalpel, just before the initiation procedure.

The filiform corrosion test was carried out according to specification DIN65472 [4.20], with a modification for the second set of samples which were subject to an initiation time above hydrochloric acid vapour of only 15 minutes instead of 1 hour (initiation times longer than 15
minutes induced extensive blistering and front corrosion instead of filiform corrosion on the samples examined).

### 4.2.2 SKP measurements

The measurements were performed at Corus Ijmuiden The Netherlands. A SKP apparatus manufactured by UBM (Germany) was used and the specimen was fixed onto a computer controlled X-Y stage. The computer controlled probe was displaceable along the Z-axis. Calibration was performed over a solution of CuSO₄ applied to pure copper. Potentials are referred to the standard hydrogen scale (V_SHE). An X x Y = 5.00 x 2.00 mm area was scanned with 40 points/mm in X-direction and 8 points/mm in Y-direction. A second scan zoomed in at the filament tip area of X x Y = 2.00 x 1.00 mm with 80 points/mm in X-direction and 20 points/mm in Y-direction. First, a surface profile of the monitored area was made by coordinated movements of the specimen and the probe. Next, the probe was moved to a distance of 50 μm away from the specimen surface for the local corrosion potential measurements. The measurements were performed at constant RH of about 100% (bottom of chamber was filled with distilled water) and at room temperature of about 22 °C. The measurements were performed on the chromate-phosphate conversion coated AA2024-T351-I samples after 1200 hours of accelerated exposure according to DIN65472 [4.20].

### 4.2.3 pH measurements

pH measurements of the electrolyte phase in the filaments are performed by removing the organic coating with the scalpel and tweezers as discussed above, immediately followed by testing the exposed electrolyte in the filament tip by narrow range pH indicator paper. The analysis was performed on cerated AA2024-T351-II samples after 1500 hours of accelerated exposure according to DIN65472 [4.20]. The resulting colour changes are compared with the colour changes after dipping pH paper in model solutions of distilled water adjusted to pH values ranging from 1.0 to 2.0 by addition of concentrated HCl (33%).
4.2.4 Time lapse video analysis

After 1500 hours of accelerated exposure according to DIN65472 [4.20], filiform corroded cerated AA2024-T351-II samples were taken directly from the exposure cabinet to the time lapse video equipment. The time lapse recordings were done with a Panasonic AG-6124 time lapse video cassette recorder. This recorder was connected to a Sony CCD camera mounted on top of a Leica Wild M420 microscope. The environmental conditions during the recordings were 20 ± 1 °C and 51 ± 1 % RH. Per 3 minutes of this ex-situ exposure, 6 seconds at real time speed were recorded while also one digital photo per 30 minutes was captured and stored on a computer, starting at the ex-situ exposure time of 0 hours. The total ex-situ exposure time was 62 hours (i.e. 186 minutes of recording and 125 digital photos in total).

4.2.5 SEM/EDX analysis

Chloride mappings by SEM/EDX analysis of filament tips on cerated AA2024-T351-II samples are made after 1500 hours of accelerated exposure, 62 hours of ex-situ exposure (time lapse video analysis) and 168 hours of subsequent accelerated exposure. The organic coating has been removed by scalpel very closely around the filaments and lifting the coating with a pair of tweezers. SEM was performed on filament tips using a Leica 360 FE field emission scanning electron microscope. EDX analysis was done at an accelerating voltage of 20 kV.

The filiform corrosion attack morphology on chromated AA2024-T351 was analysed after 1500 hours of accelerated exposure. After removal of the organic coating as described above, a subsequent cleaning procedure to remove the corrosion products has been applied, i.e. immersion of the sample in a 2% chromic trioxide (CrO₃) - 5% phosphoric acid (H₃PO₄) solution at 80°C during 5 minutes followed by a distilled water rinse. The analysis of the local corrosion attack was done in a JOEL JSM 6400F scanning electron microscope and a Link EXL EDS Analytical System.
4.3 Results

The results of the SKP measurements, pH measurements, time lapse video analysis and SEM/EDX analysis are presented in this section.

4.3.1 SKP measurements

Figure 4-1(a) and (b) show the height plot and corresponding corrosion potential distribution of a filament that developed after 1500 hours of accelerated exposure testing. The top view area of the SKP measurement is drawn schematically in the top right corner of Figure 4-1(a). The filament had started from the bottom left side of the scan area from the coating defect and had grown to a length of approximately 4 mm towards the top right corner of the scan area. Figure 4-2(a) and (b) show the height plot and potential distribution at the area of the position of the filament tip.

Figure 4-1(a) shows the elevation of the organic coating at the position of the filament to be at a maximum of 155 μm near the scratch and a more constant elevation of about 48 μm (as shown in Figure 4-2(a) in more detail) near the filament tip. This elevation of the coating at the position of the filament is the result of the formation of voluminous corrosion products, filling the filament tail.

Figure 4-1(b) shows that the corrosion potential along the delaminated zone is not constant. The filament shows two positions with relatively well pronounced negative corrosion potentials compared to the non-delaminated area, the scratch and the rest of filament tail, i.e. the very filament tip and at the end of the filament tail near the scratch. The local minimum values are –270 mV (as shown in more detail in Figure 4-2(b)) at the filament tip and –279 mV at the filament tail near the scratch. The relatively negative potential at the filament tip is very probably the result of active metal dissolution [4.6, 4.10] at this site, corresponding to the anodic site in the well-accepted theory of anodic undermining on aluminium based substrates, as presented in Chapter 1. The anodic site near the scratch could be the result of the accidental presence of a large salt particle at that position, resulting in a local aggressive environment leading to active metal dissolution at that specific spot. At the scratch and in the filament tail more positive corrosion potentials are found. Local maximum values of 285 and 75 mV are found in the scratch and filament tail respectively. These potential values are most probably caused by the presence of corrosion products at these sites, which have been formed during the long corrosion times, hereby inhibiting the anodic metal dissolution [4.6].
Figure 4-1: Scanning Kelvin Probe measurements of a filament on AA2024-T351: (a) shows the height plot and (b) shows the potential distribution of the scanned area ($X \times Y = 5.00 \times 2.00$ mm)
Figure 4-2: Scanning Kelvin Probe measurements of a filament tip on AA2024-T351: (a) shows the height plot and (b) shows the corresponding potential distribution ($X \times Y = 2.00 \times 1.00$ mm); the exact position of the filament tip in the scanned area of Figure 4-1 is shown in (a).

Such a behaviour is also frequently found in aqueous corrosion studies [4.6]. In addition, at the back of the filament head (or the beginning of the filament tail) the higher corrosion potentials are probably caused by the oxygen reduction reaction at the location of the cathodic
Mechanistic investigation into filiform corrosion on AA2024-T351

site [4.10], according to the anodic undermining mechanism. The interpretation of the absolute corrosion potentials at the position of the filament was not the main interest at this point of the study. However, it is encouraging that the corrosion potential values at the very filament tip and just behind it are similar to the recently reported values by Schmidt et al. [4.10] on AA2024-T3, both in an absolute and relative sense, taken into account different experimental procedures. Schmidt et al. [4.10] reported a local minimum value of −315 mV at the filament tip and −15 mV (relative potential difference: 300 mV) just behind it, while the present study shows values of −270 mV and 75 mV (relative potential difference: 345 mV) respectively.

It is evident that the SKP is an effective tool in the detection of intact and filiform corroded zones on coated aluminium alloys, as well as the detection of active and inactive sites in the filiform corroded zones. Relatively negative corrosion potential values are the result of active metal dissolution at those sites, whereas relatively positive corrosion potential values indicate the presence of passive corrosion products or the occurrence of reduction reactions, such as oxygen reduction.

4.3.2 pH measurements

Figure 4-3(a) shows two filaments underneath the transparent coating, which is later removed with a scalpel and tweezers as described in the experimental section of this Chapter (Figure 4-3(b)). Immediate testing of the electrolyte in the filament tips with narrow range pH indicator paper (Figure 4-x(c)) and comparison of the colour changes with those after dipping of the pH indicator paper in model solutions ranging from 1.0 to 2.0 (Figure 4-3(d)), confirms the pH values in these filament tips to be 1 to 2. No clear indication of pH values at the back of the head or the tail could be derived with this analysis procedure probably due to low liquidity conditions at these sites, indicating that the filament tail is filled with dry corrosion products.
Figure 4-3: pH measurements in the filament tip on AA2024-T351 with narrow range indicator paper. (a) shows two filaments underneath a transparent organic coating. (b) shows these filaments after coating removal and (c) shows the indicator paper of the corresponding area after electrolyte testing of the filaments. (d) shows the colours of the indicator paper after dipping this in the model solutions with pH values of 1.0, 1.5 and 2.0.

4.3.3 Time lapse video analysis

In this section, parts of the time lapse video recordings, edited and produced by Mol et al. [4.21], are discussed.

Figure 4-4 shows gas evolution in a filament tip on AA2024-T351 after having taken the sample out of the accelerated exposure test for 2.5 hours. Due to hydration of aluminium ions, local acidification at the anodic site takes place and a secondary cathodic reaction, the reduction of hydrogen ions, can occur. While no chemical analysis of these bubbles is performed, these bubbles are taken to be hydrogen bubbles from the $\text{H}^+$-reduction reaction. The filament tips analysed showed a gradual decrease of the number and size of the hydrogen bubbles with ex-situ exposure time. This was probably the result of the fact that the samples were taken out of the exposure cabinet, controlled at 40 °C and 82 % RH, to the time lapse video equipment with environmental conditions during the recordings at 20 °C and 51 % RH. This could have resulted in a decrease of the anodic and cathodic reaction rate and partial drying out of the filament electrolytes with time during the recordings.
Figure 4-4: Filament tip on AA2024-T351 showing hydrogen evolution through the transparent organic coating (Schematic position of the hydrogen bubbles in the tip are shown in the top left corner). Ex-situ exposure time 2.5 hours.

Figure 4-5 shows six snapshots from the time lapse sequence of a filament tip on cerated AA2024-T351. These digital photos were taken at ex-situ exposure times of 0, 12, 24.5, 37, 49.5 and 62 hours respectively. The thin dotted ellipses indicate the approximate position of the dark electrolyte in the filament tip in which hydrogen evolution, as shown in Figure 4-4, is observed. Corrosion products can be observed in the filament tail, trailing the filament tip. It can be seen that the voluminous corrosion products are formed close to the very tip of the filament. The electrolyte is believed to include the anolyte at the front of the filament tip. This anolyte is shown to be acidic by the pH measurements and the hydrogen evolution observations presented in the previous and this section respectively. In the next section this area is shown to have a very high chloride concentration too.
Figure 4-5: Filament tip on AA2024-T351 showing a stepwise filament propagation and transport of species in the filament head. (a) through (f) are snapshots from the time lapse video after ex-situ exposure times of 0, 12, 24.5, 37, 49.5 and 62 hours.
As shown in Figure 4-5(a) through (d), the surface area covered with the anolyte decreases with time. This could be the result of lower corrosion reaction rates and partial drying out of electrolyte in the time lapse video recording environment of 20 °C and 51 % RH, compared to the conditions of 40 °C and 80 % RH in the accelerated exposure cabinet. After approximately 35 hours of ex-situ exposure, a blister type of delamination takes place at the front of the filament tip at the position of the anolyte. Then subsequent transport of the dark (acidic, chloride-rich) electrolyte to the new filament tip takes place. The tip propagation is not a continuous but a stepwise process. This propagation mechanism results in a recurrent necking or closely packed blister propagation pattern along the filament tail. The observation of recurrent necking supports an apparent stepwise filiform propagation [4.15]. The width of the new filament tip of ~0.27 mm is smaller than the width of the filament tail of ~0.60 mm, which is formed in the accelerated exposure cabinet, probably as a result of the lower RH at which the time lapse video recordings were performed.

It must be noted that the indicated positions of the anolyte as a function of ex-situ exposure time are estimations and not absolute. This is confirmed by the fact that after re-exposition in the accelerated exposure test, a double headed filament, as shown in Figure 4-6 of the next section, was formed with the position of the second filament tip below the position of the new filament tip as discussed in this part. This could be the case when some of the acidic chloride-rich anolyte was left behind in the old filament tip and not completely transported yet to the new filament tip before the re-exposition.

4.3.4 SEM/EDX analysis

Further qualitative analysis into the composition of the electrolytes is done using SEM/EDX. Especially the high chloride concentration at the very tip of the analysed filaments has proven to be evident as shown in Figure 4-6. Figure 4-6(a) shows a double headed filament on cerated AA2024-T351 and Figure 4-6(b) shows the corresponding chloride-mapping: evident is the high chloride concentration in the very tips of both filament heads (Figure 4-6(c) and (d) are the chloride mappings of the lower and upper filament tip respectively at higher magnification).
Figure 4-6: SEM/EDX chloride-mapping in the filament tips of a double-headed filament on a cerated AA2024-T351 substrate (light grey areas correspond with high chloride concentrations). Analysis was performed after 1500 hours of accelerated exposure, 62 hours of ex-situ exposure (time lapse video analysis) and 168 hours of subsequent accelerated exposure.

According to the anodic undermining theory these sites correspond to the anodic site, as presented in Chapter 1. In chloride mappings further down the tail and even in the area of the original coating defect no or very low chloride concentrations are detected, indicating that very little chloride is incorporated in the corrosion products. Apparently, the chloride ions mainly travel with the filament tip providing local electroneutrality conditions for filament growth and continuous participation of a more or less constant number of chloride ions in the substrate surface attack.

The SEM/EDX analysis proves to be an effective tool in the analysis of the type of attack underneath filaments on filiform corroded samples. The corrosion attack shows a heterogeneous corrosion attack underneath the filament. Figure 4-7(a) shows a top view of the filiform corrosion attack down a filament tail on a chromated AA2024-T351 sample (BSE mode). Arrow 1 indicates clear examples of aluminium matrix dissolution around intermetallic particles. Although no pre-corrosion analysis of the same area has been performed, also sites can be observed in Figure 4-7(a), where intermetallics could be dissolved or undercut by dissolution of the surrounding aluminium matrix and washed off after cleaning and rinsing. With EDX analysis, intermetallic phases left behind in the tail are identified as Al-Cu and Al-Si-Fe-Mn and Al-Cu-Mg phases. The non-corroded region at the bottom of Figure 4-7(a) shows no sign of attack from the pretreatment or the corrosion product removal procedures, so it can be assumed that the observed morphology was created during the corrosion process. Figure 4-7(b) shows more types of local filiform
corrosion attack in the very tip of a filament on chromated AA2024-T351.

Figure 4-7: Top view SEM analysis of the filiform corrosion attack on chromated AA2024-T351
Arrow 2 indicates local cube-shaped etch pitting corresponding with attack in a preferential crystallographic orientation. Such differences in the pitting behaviour with grain surface orientation have been reported previously, both for pitting corrosion studies [4.22-4.25] and filiform corrosion studies [4.15, 4.26]. More severe pitting can also be observed in the filament tip as indicated by arrow 3. Grain boundary attack is indicated by arrow 4 corresponding with preferential grain boundary phase dissolution, probably because of the presence of a more anodic zone (alloying element depletion) compared to the rest of the matrix and/or intergranular precipitates.

4.4 Discussion

Having presented the results of the mechanistic investigations into the filiform corrosion on AA2024-T351, now a general and local mechanism of filiform corrosion attack is presented. Furthermore the role of microstructural variations during filiform corrosion propagation is discussed in this section. A schematic representation of filiform corrosion propagation on aluminium based substrates is presented in Figure 4-8.

\[ \text{H}_2\text{O, O}_2 \]

\[ \text{Anodic site} \quad \text{Cathodic site} \quad \text{Coating defect} \]

\( \uparrow \) = Anodic Al dissolution reaction  
\( \Theta \) = Cathodic \( \text{O}_2 \) reduction reaction  
\( \circ \) = Cathodic \( \text{H}^+ \) reduction reaction (\( \text{H}_2 \) bubbles)

**Figure 4-8:** General mechanism of filiform corrosion on aluminium based substrates according to the anodic undermining mechanism.
The Scanning Kelvin Probe measurements have shown a clear anodic site, suggesting active metal dissolution, at the very tip of the filament, and a trailing area with a less negative corrosion potential. Macrographic pictures taken through the organic coating show the formation of corrosion product close to the very tip of the filament. These observations may support the recently proposed model of Spoelstra [4.17] that the actual cathodic area is positioned at the front of the area where corrosion products are deposited. This would suggest that a membrane dividing two liquid phases, the anolyte and the catholyte, similar to the membrane of solid corrosion products reported by Van der Weijde et al. [4.27] for cathodic delamination on iron based substrates, may not be present in the case of filiform corrosion on aluminium based substrates. A membrane or more generally a clear separation of strict anodic and cathodic sites could not be observed during the present study.

The time lapse video sequences show that hydrogen evolution takes place at the tip of the filament, i.e. the anodic site. This, together with the pH measurements and the chloride mappings in the filament tip, shows that the anolyte is an aggressive chloride-rich acidic electrolyte, promoting local metal dissolution.

Following these observations it can be concluded that at the anodic site, aluminium dissolution takes place according to Equation 4-1. Due to hydration of aluminium ions, local acidification of the anolyte takes place and a secondary cathodic reaction, the reduction of hydrogen ions as shown in Equation 4-2, can occur:

\[
\text{Al} + 2 \text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Al(OH)}_2\text{Cl} + 2 \text{H}^+ + 3 \text{e}^- \quad (4-1)
\]

\[
2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \quad (4-2)
\]

At the cathodic site, trailing the anodic site, the primary cathodic reaction, the reduction of oxygen, takes place:

\[
\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad (4-3)
\]

Preceding the electrochemical reactions shown above, the chloride containing acidic anolyte provides the necessary condition for chemical breakdown of the protective coating-substrate interface (i.e. natural oxide or pretreatment layer), exposing the substrate microstructure. This process, includes the chloride release from transitory hydroxychloride complexes providing
electroneutrality conditions in the anolyte and continuous participation of a more or less constant number of chloride ions in the substrate surface attack. However, some entrapment of chloride in the corrosion product filled filament tail could contribute to a stagnation of filament growth rate after considerable exposure times [4.12, 4.15-4.17], in addition to a decrease of the oxygen concentration gradient with increasing filament lengths [4.17-4.19].

Now, the local attack mechanism during filiform corrosion propagation is discussed taking into account the effects of microstructural variations in the substrate. Local corrosion phenomena at the anodic site are presented schematically in Figure 4-9.

Figure 4-9: Schematic representation of local corrosion phenomena and the role of microstructural variations in the substrate. (a) and (b) show the cases of the presence of a cathodic and anodic particle respectively.
As presented in Chapter 1, traditionally, local corrosion processes on aluminium based substrates have been attributed to progressive interactions between the matrix and clustered particles [4.28, 4.29]. Recent studies [4.30-4.33] of particle-induced corrosion indicate that particles may be broadly divided into particles which are cathodic or anodic with respect to the aluminium matrix. A schematic representation of the localised corrosion processes during filiform corrosion in case of the presence of cathodic or anodic particles is presented in Figure 4-9(a) and (b) respectively. Observations by other researchers [4.30, 4.31] show that cathodic particles tend to promote dissolution of the surrounding matrix and the accompanying reduction reaction of hydrogen ions will preferentially occur on the cathodic particles. Such dissolution of the matrix around particles is observed also for filiform corrosion on AA2024-T351, as shown in section 4.3.4. Figure 4-9(a) shows that the local aluminium dissolution at the anodic site around the particles results in an increased cathodic surface area exposed to the electrolyte as the localised corrosion proceeds. This increase of exposed cathodic area leads to a further increase of the corrosion reactions at the anodic site, but also an increase of the overall cathodic reaction at the cathodic site, because the prior anodic site becomes the cathodic site when filiform corrosion proceeds. Progressive anodic dissolution of the surrounding matrix and resultant oxide formation may eventually lead to decoupling of the cathodic particles from the alloy, leaving them electrically isolated from the matrix. Under such circumstances, the dissolution of these particles is dictated by their individual corrosion potentials. It might also be possible that, even when the particle is still electrically coupled to the matrix, some galvanic activity, between different alloying elements of the particle may prevail, leading to some preferential dealloying of the particle. However, it is believed that this internal galvanic coupling is of minor importance for cathodic particles.

In case anodic particles are present, preferential dissolution of such particles will take place, possibly leading to complete dissolution of the particle, as shown in route I in Figure 4-9(b). The characterisation of particles as strictly cathodic or anodic, however, is not precise. In case a particle is anodic to the surrounding matrix, some elements may dissolve preferentially from this particle, as shown in Figure 4-9(b), route II. This preferential dissolution of constituent elements eventually leads to surface enrichment of certain noble elements of the particle. An example of such change of electrochemical nature has previously been reported by Chen et al. [4.31] and Buchheit et al. [4.34]. They observed that the S phase particle (Al₃CuMg), which is anodic with respect to the matrix (see Table 1-1), undergoes dealloying with preferential dissolution of magnesium and aluminium,
leaving a copper-rich sponge, which becomes more noble as the dealloying proceeds. In this way, the electrochemical nature of this particle may change from anodic to cathodic. From this discussion and the results presented earlier, it can be argued that the electrochemical nature of particles present in aluminium alloys, their concentration and their distribution are of major importance for the filiform corrosion propagation rate of these alloys. The kinetics of the cathodic reaction on cathodic particles is not a constant but varies with the type of particle. Not only the overpotential of particles compared to the surrounding matrix is of importance for the local corrosion phenomena, but especially the kinetics of the corrosion reactions at these particles. High cathodic reaction rates on the particles will result in a high anodic dissolution rate of the surrounding matrix, as shown schematically in Figure 4-10(a). At high dissolution rates the corroded zone is likely to cover a larger area of the substrate surface. In the case of the presence of anodic particles, the anodic dissolution reaction is confined to the particle itself and the corroded zone does not spread over the substrate surface.

The effect of the concentration of cathodic or anodic particles and their distribution is presented schematically in Figure 4-11. For a high concentration and/or fine distribution of particles it is likely that other ‘fresh’ cathodic particles are more rapidly reached by the corroded zone around these particles, which in turn will participate in the substrate matrix dissolution, as shown in Figure 4-11(a). In this way, a large cathodic surface area will participate in the matrix dissolution process for a high concentration and/or fine distribution of cathodic particles. The increased cathodic area will therefore lead to rapid spread of the corrosion front and thus a high filiform corrosion propagation rate. The discontinuous nature of the participation of ‘fresh’ cathodic surfaces, as well as the fallout of particles by undercutting, results in a non-constant filiform corrosion front propagation rate. In addition, rapid matrix dissolution will lead to a high regeneration rate of chloride ions after dissolution of the transitory hydroxy-chloride compounds and a high deposition rate of voluminous corrosion products.
Figure 4-10: Schematic representation of local corrosion phenomena and the effect of the kinetics of the local corrosion reactions, i.e. type of particle. (a) and (b) show the cases of the presence of a cathodic and anodic particle respectively.

The build up of corrosion product and the resulting mechanical pressure at the front of a filament will finally lead to coating delamination when the mechanical pressure exceeds the bonding strength between the organic coating and the substrate surface. In general, a stressed coating can delaminate from the substrate if the stored, recoverable elastic energy in the coating layer is larger than the energy required for debonding [4.35]. The total amount of energy needed to debond a coating from a substrate per unit of area is the energy
release rate $G_{\text{c,adh}} [4.35]$. If the organic coating has the ability to form large deformation zones in the surroundings of the filament tip by energy dissipation, the onset of unstable and rapid debonding is postponed [4.36]. The unstable and rapid growth of the delamination front will stop when the mechanical pressure has decreased, by the increase of filament tip volume, down to the bonding strength of the coating-substrate interface. Such a discontinuous mode of coating delamination would explain the stepwise growth of the filament tip as observed during the time lapse video analysis. The relative contributions of the (electro)chemical undermining of the coating at the filament tip and the mechanical debonding resulting from the corrosion product lifting force respectively are likely to be influenced by the adhesion properties of the organic coating to the (pretreated) substrate surface [4.15]. When comparing the filiform corrosion propagation properties of coated systems in case reproducible, similar and well adhering organic coatings and chemical pretreatments are applied, the differences in average filiform corrosion propagation rates can be attributed to differences in the microstructure of the substrates under investigation, leading to different average anodic undermining rates, with the mechanical stepwise debonding mechanism as a second order effect. In case of bad adhesion between the organic coating and the substrate surface the low bonding strength may predominantly influence the filiform corrosion propagation mode and rate: ultimately, at very low and non-constant bonding strength over the substrate surface, front corrosion and a wide scatter of filiform corrosion test results can be observed, independent of the microstructure of the underlying metal.

In the case of the presence of anodic particles, rapid matrix dissolution is less likely, as schematically presented in Figure 4-11(b). The anodic particle will dissolve preferentially leaving behind a relatively homogeneous substrate surface. In the absence of heterogeneities in the substrate surface, localised corrosion by the formation of microgalvanic couples will not occur, leading to a relatively low substrate surface attack rate, also not very much depending on the concentration of the anodic particles.
Figure 4-11: Schematic representation of local corrosion phenomena and the effect of the particle concentration. (a) and (b) show the cases of the presence of a cathodic and anodic particle respectively.

The accelerated filiform corrosion exposure tests presented in Chapter 2, show a clear compositional effect on the filiform corrosion behaviour of the tested substrates. The trend of an increasing average filament length with the alloying concentration is especially clear for the highly susceptible Al-Cu binary alloys and also for the degreased Al-Si alloys. This
is in contrast with the degreased Al-Zn and Al-Mg alloys which show no or little significant increase in average filament length with solute content. The different correlations for the Al-Cu and Al-Zn alloys are explained from the electrochemical response, i.e. corrosion reaction kinetics, to local variations of the substrate composition, as shown in Chapter 3. The Al-Cu alloys show an increase of the cathodic and the anodic reaction rates with Cu concentration. For the Al-Zn alloys a more constant overall cathodic and anodic reaction rate as a function of the Zn concentration is observed. This explains the increasing average filament length with Cu concentration and the more constant average filament length with increasing Zn concentration after accelerated exposure testing.

The mechanism presented in this section, implicitly supports the variation of propagation rate with type and concentration of alloying element as presented in Chapter 2. Selective dissolution of the aluminium matrix in Cu containing alloys leads to the formation of cathodic Cu-rich zones or particles promoting the cathodic reduction reaction at these sites. The accompanying high dissolution rate of the surrounding aluminium matrix promotes the filiform corrosion to propagate and coalescence of pits will further attack the substrate and undermine the organic coating at the front of the filament. In the absence of such distinct cathodic phases, as for example the case for the Al-Zn and Al-Mg binary alloys, the cathodic reaction is not stimulated and the substrates prove to be much less susceptible to filiform corrosion and relatively independent of the alloying concentration. Anodic (Zn or Mg containing) phases may dissolve, leaving pits in the surface of a more homogeneous aluminium rich matrix. Therefore, these substrates are less susceptible to localised attack due to the lack of noble particles.

4.5 Conclusions

The Scanning Kelvin Probe confirms the classical anodic undermining mechanism to be applicable for filiform corrosion on aluminium based substrates. It clearly distinguished delaminated areas from intact areas and showed the anodic site to be present at the very tip of the filament. pH measurements, time lapse video analysis of hydrogen evolution and SEM/EDX chloride mappings showed the anolyte be at low pH values of 1-2 and to be very rich of chloride ions, attributing to the attack of the underlying substrate. SEM/EDX analysis of filiform corrosion attack showed preferential attack of the aluminium rich matrix around cathodic particles. The local substrate attack model
presented in this chapter shows in particular the importance of the presence of cathodically active phases and their concentration and distribution in the substrate surface for filiform corrosion propagation, confirming the observations reported in the two previous chapters. The high dissolution rate of the aluminium matrix, stimulated by a high cathodic reaction rate at the position of noble particles, promotes the filiform corrosion to propagate by anodic undermining of the organic coating at the filament tip. The kinetics of the cathodic reactions vary with the type of particle and the total surface area of active cathodic phases are determined by their concentration and distribution. The discontinuous nature of the participation of ‘fresh’ cathodic surfaces, as well as the fallout of particles by undercutting, results in a non-constant filiform corrosion front propagation rate on a microscale. In addition, rapid matrix dissolution will lead to a high deposition rate of voluminous corrosion products. The resulting mechanical pressure at the front of a filament may finally lead to coating delamination when the mechanical pressure exceeds the bonding strength between the organic coating and the substrate surface. In general, a stressed coating can delaminate from the substrate if the stored, recoverable elastic energy in the coating layer is larger than the energy required for debonding. If the organic coating has the ability to form large deformation zones in the surroundings of the filament tip by energy dissipation, the onset of unstable and rapid debonding is postponed. The unstable and rapid growth of the delamination front will stop when the mechanical pressure has decreased, by the increase of filament tip volume, down to the bonding strength of the coating-substrate interface. The relative contributions of the (electro)chemical undermining of the coating at the filament tip and the mechanical debonding resulting from the corrosion product lifting force respectively are likely to be influenced by the adhesion properties of the organic coating to the (pretreated) substrate surface. When comparing the filiform corrosion propagation properties of coated systems in case reproducible, similar and well adhering organic coatings and chemical pretreatments are applied, the differences in average filiform corrosion propagation rates can be attributed to differences in the microstructure of the substrates under investigation, leading to different average anodic undermining rates, with the mechanical stepwise debonding mechanism as a second order effect.

In the absence of such cathodic phases, the cathodic reaction is not stimulated and the substrates prove to be much less susceptible to filiform corrosion. Active anodic phases may dissolve, leaving pits in the surface of a more homogeneous aluminium rich matrix, being less susceptible to localised attack due to the lack of noble particles.
References

4.7 M. STRATMANN and A. LENG, *Farbe und Lack* 100 (1994) p. 93
4.15 H. LETH-OLSEN, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1996)
4.20 Deutsches Institut Für Normung e.V., Number 65472: Filiform corrosion test of coatings on aluminium alloys, draft (1989)
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4.26 A. AFSETH, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1999)


Filiform corrosion of model substrates with synthetic chemical and topological defects

Filiform corrosion experiments have been performed on two sets of coated aluminium AA1060 sheet containing synthetic copper and magnesium enrichments respectively. For the first set of samples, line shaped synthetic defects were generated by sputtering copper-rich tracks and a subsequent thermal treatment to stimulate diffusion of copper into the aluminium matrix. The surface treatments applied prior to coating the sample with an airdrying organic clearcoat, cover simple degreasing and technically well-proven chemical pretreatments. The second set of samples cover Mg-rich defects which were produced by ion implantation. Also the results of an investigation into the effects of surface texture on filiform corrosion propagation for two grades of AA2024-T351 are presented in this chapter.

5.1 Introduction

In the previous chapters it was shown that filiform corrosion is a complex phenomenon
involving contributions from the environmental conditions, the organic coating, the coating-substrate interface and the substrate surface. The hypothesis that the initiation of blisters and filament propagation on the one hand and the general corrosion properties of the aluminium alloy on the other are closely related is very important in the present investigation. At a coating defect the metal substrate is directly exposed to the humid atmosphere. Initiation of corrosion may then start at local irregularities in the oxide layer. Such irregularities are related to the presence of alloying elements either in solid solution or as intermetallic phases in the alloy. These local differences in composition influence the quality of the oxide layer, and as a consequence the protective properties. In particular, when copper-rich phases are present, the cathodic reaction preferably occurs at these particles and stimulate corrosion. Experimental results, both presented in this thesis and in the literature [5.1-5.13] clearly indicate that the filiform corrosion parameters, such as site density and propagation rate, strongly depend on the microstructure of the alloy.

The local substrate attack model presented in the previous chapter demonstrated the importance for filiform corrosion propagation of cathodically active phases being present in the substrate surface. The high dissolution rate of the aluminium matrix, stimulated by a high cathodic reaction rate at the position of noble particles, promotes the filiform corrosion to propagate by anodic undermining of the organic coating at the filament tip. In the absence of such distinct cathodic phases, the cathodic reaction is not stimulated and the substrates prove to be much less susceptible to filiform corrosion, almost irrespective of the alloying concentration. Anodic phases on the other hand may dissolve, leaving pits in the surface of a more homogeneous aluminium rich matrix. Therefore, substrates containing anodic phases are less susceptible to localised attack.

Generally, the influence of alloying elements can be investigated by determining the filiform corrosion properties of technical aluminium alloys, using a statistical analysis of the results. Regardless of the stochastic-like appearance of the local attack, the number of initiations and average filament lengths are related to general alloy composition and temper conditions. However to obtain a clear insight into the mechanism of filiform corrosion and the substrate effects on a microstructural level, it is necessary to analyse the filiform corrosion properties of well-defined and reproducible model substrates, containing synthetic defects. In this chapter the role of synthetic copper- and magnesium-rich impurities in the aluminium substrate surface on filiform corrosion is examined. The aim of this investigation is to study the influence of the presence of more noble (copper) and
Filiform corrosion of model substrates with synthetic chemical and topological defects

less noble (magnesium) macro-enrichments respectively, on the filiform corrosion initiation and propagation behaviour of coated commercially pure aluminium model substrates.

For the first set of samples, these synthetic defects were generated by depositing copper-rich tracks via a magnetron sputter process and a subsequent thermal treatment to stimulate diffusion of copper into the aluminium matrix. Three levels of initial sputter layer thickness and three thermal treatment procedures were investigated: the samples were subjected to either a solution heat treatment only or a solution heat treatment plus a precipitation or overaging treatment. The chemical pretreatments were varied from degreasing only to two different chromate based conversion coatings treatments. To understand the observed effect of the copper-rich tracks on filiform corrosion, additional experiments were performed where copper pins were inserted in holes drilled in an AA2024 substrate.

The second set of samples involves magnesium-rich defects which were produced by ion implantation. Three levels of magnesium concentration were investigated. No additional heat treatment was applied and only degreased samples were investigated.

The filiform corrosion susceptibility of aluminium alloys subjected to a mechanical grinding procedure has gained technological interest in automotive applications as grinding is commonly used as part of an assembly and repair service prior to pretreatment for painting [5.3, 5.14]. From earlier research work it is already known that the actual propagation direction of the filaments is influenced by the surface topology. Filaments typically follow the rolling direction [5.3, 5.4, 5.6, 5.7, 5.15, 5.16] or scratch lines on a ground surface [5.3, 5.4, 5.17]. If a pronounced topography is removed either by mechanical polishing, etching, anodising or sandblasting [5.3, 5.4, 5.6], the directionality is lost and a more random filiform corrosion growth direction takes over. It is reported that mechanical grinding of aluminium surfaces prior to coating give no improvement of the filiform corrosion susceptibility compared to degreasing [5.3, 5.4, 5.15, 5.17, 5.18]. It is even reported that dry sanding of aluminium alloy surfaces increased the filiform corrosion susceptibility significantly, attributed to the presence of embedded impurities at the substrate surface after sanding [5.14]. The detrimental effects of sanding could be reduced by proper lubrication during sanding. An acid or alkaline etching procedure to remove the mechanically affected surface layer or a reactive pretreatment is necessary to remove the disturbed surface layer and render the surface highly resistant to filiform corrosion [5.3,
5.4]. Also mechanically polished surfaces were shown to be less filiform corrosion susceptible than as-rolled or mechanically ground surfaces [5.3]. Although effects of grinding or working may be due to an indirect chemical effects, the promotion and steering of the growth direction may also be attributed to geometrical effects. The effect of rolling and grinding marks on growth direction is studied in this chapter in some detail. Furthermore, specific surface patterns have been designed with the aim of prematurely blocking filiform growth, and their effectiveness has been examined.

5.2 Experimental

In the present investigation, filiform corrosion properties of model substrates were investigated on a laboratory scale by accelerated exposure tests. Corrosion experiments were performed on commercially pure aluminium sheet containing synthetic chemical defects. A strict procedure was followed to obtain reproducible model substrates.

5.2.1 Preparation of model substrates containing copper defects

As illustrated in Figure 5-1, copper-rich tracks were magnetron sputtered in a high vacuum chamber on commercially pure AA1060-H24 (Tables 5-1 and 5-2).

![Figure 5-1: Schematic representation of an artificially copper-enriched AA1060-H24 model substrate](image)
Filiform corrosion of model substrates with synthetic chemical and topological defects

A chemical polishing pretreatment (Table 5-3) was used to provide a well-defined base substrate surface before controlled deposition and diffusion procedures.

**Table 5-1:** XRF-analysis of the chemical composition of the base aluminium substrate AA1060-H24 in wt-%

<table>
<thead>
<tr>
<th>Element</th>
<th>AA1060-H24 as-rolled</th>
<th>AA1060-H24 chemically polished</th>
<th>AA1060-H24 chemically polished and mechanically surface treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.25</td>
<td>0.11</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe</td>
<td>0.22</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>Mg</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Other</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Al</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

**Table 5-2:** XRF-analysis of the chemical composition of the copper-rich sputter target in wt-%

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu sputter target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.77</td>
</tr>
<tr>
<td>Ni</td>
<td>0.23</td>
</tr>
<tr>
<td>Other</td>
<td>&lt; 0.14</td>
</tr>
<tr>
<td>Cu</td>
<td>balance</td>
</tr>
</tbody>
</table>

Diffusion of the deposited copper-rich tracks into the base aluminium substrate was induced by heat treating the specimens, as shown in Table 5-4. Three different thermal treatment procedures were used to compare different model temper conditions. In order to prevent the specimens from oxidation during the thermal treatment, the specimens were packed in stainless steel envelopes and flushed with high purity nitrogen gas before sealing.
Table 5-3: Chemical polishing procedure details

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>H₃PO₄ (85 %, M=98,00 g/l): 93 vol-%</td>
</tr>
<tr>
<td></td>
<td>HNO₃ (65 %, M=63,01 g/l): 7 vol-%</td>
</tr>
<tr>
<td>Temperature</td>
<td>80 °C</td>
</tr>
<tr>
<td>dwell time</td>
<td>10 minutes</td>
</tr>
</tbody>
</table>

Table 5-4: Deposition and annealing conditions of Al-Cu model substrates

<table>
<thead>
<tr>
<th>Deposition conditions</th>
<th>¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sputter thickness</td>
<td>0 nm</td>
</tr>
<tr>
<td></td>
<td>50 nm</td>
</tr>
<tr>
<td></td>
<td>200 nm</td>
</tr>
<tr>
<td></td>
<td>1000 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution heat treatment</td>
<td>535 °C, 25 minutes, cold water quench</td>
</tr>
<tr>
<td>precipitation heat treatment</td>
<td>190 °C, 8 hours</td>
</tr>
<tr>
<td>overaging heat treatment</td>
<td>190 °C, 48 hours</td>
</tr>
</tbody>
</table>

¹) Balzers BAE250T High Vacuum magnetron sputter unit
²) Precipitation and overaging heat treatment are preceded by the solution heat treatment

Finally the specimens were slightly mechanically abraded (FEPA P4000 SiC paper) and polished (3 μm) in the copper-rich line defect direction, to remove residual copper-oxides and to obtain a constant roughness and macroscopic morphology over the total model substrate surface. The chemical composition of the reference AA1060-H24 samples as analysed by XRF is presented in Table 5-1. This table shows that Si and Fe are the major impurity elements in the commercially pure AA1060-H24 samples tested. The Si-concentration significantly decreases from 0.25 to 0.11 wt-% after chemically polishing the surface, possibly by preferential dissolution of components during the chemical polishing treatment. The Si-concentration is increased from 0.11 to 0.38 wt-% after the mechanical grinding and polishing procedure, probably related to embedding of SiC-particles in the surface layer after the grinding step. The Fe-concentration shows a more constant level of
Filiform corrosion of model substrates with synthetic chemical and topological defects

0.20-0.22 wt-%. Roughness measurements as presented in Table 5-5 indicate an increasing level of surface smoothness after chemical polishing and a consequent mechanically surface treatment respectively, both in rolling direction and perpendicular to it. As can be expected from the presence of initial rolling marks, the surface roughness in rolling direction is smaller than in the transverse direction. The absolute difference between the substrate surface roughness in both direction decreases with the level of surface treatment. The presence of surface treatment marks still present after chemical polishing and mechanical surface treatment is shown by the AFM measurements in Figure 5-2.

Table 5-5: Roughness measurements of the AA1060-H24 model substrate surfaces: $R_a$ values in $\mu$m (RD: rolling direction; TD: transverse direction)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as-rolled</td>
<td>chemically</td>
<td>chemically polished and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polished</td>
<td>mechanically surface treated</td>
</tr>
<tr>
<td>RD</td>
<td>0.17</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>TD</td>
<td>0.29</td>
<td>0.21</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Figure 5-2: AFM measurements of the model substrate surface after chemical polishing and mechanical surface treatment revealing the presence of surface treatment marks at the surface. Scan area: (a) 50 x 50 $\mu$m, (b) 10 x 10 $\mu$m.

The copper-rich zones are analysed by optical microscopy and EPMA analysis. Figures 5-3
and Figure 5-4 show examples of copper-rich diffusion zones in cross-section of model substrates with an initial sputter layer thickness of 200 nm and 1000 nm respectively.

Figure 5-3: Optical micrograph of an artificially Cu-enriched diffusion zone on a AA1060-H24 model substrate with an initial sputter layer thickness of 200 nm after heat treatment at 535 °C for 25 minutes and a cold water quench, followed by 190 °C for 14 hours.

Figure 5-4: Optical micrographs of an artificially Cu-enriched diffusion zone on a AA1060-H24 model substrate with an initial sputter layer thickness of 1000 nm after heat treatment at 535 °C for 25 minutes and a cold water quench, followed by 190 °C for 48 hours. (b) shows a part of the diffusion zone in more detail.

Figure 5-3 and 5-4 show an irregular cross-sectional shape and maximum depth of the diffusion zone at the surface of the line defect.

An indication of Cu-concentration as a function of diffusion depth can be deduced from Electron Probe X-Ray Micro Analysis (EPMA) results, as shown in Figure 5-5.
The depth of diffusion equals the lateral spread of the Cu-rich tracks due to thermal treatment, i.e. there is no significant diffusion of copper to the areas in between the tracks.

\[
\begin{align*}
\text{Cu concentration} & \quad [\text{at-\%}] \\
0 & \quad 0.0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \\
\text{Diffusion depth} & \quad [\text{micrometer}] \\
0 & \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70
\end{align*}
\]

\textit{initial sputter thickness:} \quad \blacktriangle 200 \text{ nm}; \quad \blacklozenge 1000 \text{ nm}; \quad \text{overaging heat treatment}

**Figure 5-5:** EPMA-analysis of Cu-concentration as a function of diffusion depth

In the present investigation, three different pretreatment procedures were applied, varying from solvent cleaning with ethanol only to the applications of two types of chromate based conversion coatings, prior to coating. Conversion coating I (CC-I) is a chromate-phosphate conversion coating and conversion coating II (CC-II) is a chromate conversion coating. It is important to realize that the two conversion coatings were neither selected nor optimized nor tested for their effectiveness in preventing filiform corrosion from developing.

A transparant air-drying epoxy/amine based coating has been developed in close cooperation with Akzo Nobel Coatings Holland. The coating was selected on the basis of initial adhesion tests, wet adhesion tests and blister formation after two weeks immersion in demineralized water at room temperature, adhesion tests and blister formation after two weeks exposure to 100 % RH at 40 °C and also visibility of filiform corrosion during accelerated exposure tests.

To demonstrate local corrosion potential variations over the sample surface resulting from the presence of the copper-rich line defects, Scanning Kelvin Probe (SKP) measurements were performed. The measurements were performed at Corus IJmuiden The Netherlands.
More detailed information about this SKP technique and the experimental details are presented in sections 4.1.1 and 4.2.2 respectively.

Figure 5-6: Scanning Kelvin Probe line scan (length = 50 mm) over coated AA1060 surfaces without copper-rich line defects (a) and with copper-rich line defects (b) and (c): (b) and (c) show the corrosion potential scans of the model substrates covered with CC-I and CC-II respectively. The vertical dashed lines in (b) and (c) indicate the positions of the line defects. All scans are performed after the filiform corrosion tests over unattacked areas.

The measurements were performed at constant RH of about 100% (bottom of chamber was filled with distilled water) and at room temperature of about 22 °C on the coated samples after 1000 hours of accelerated exposure according to DIN65472 [5.19]. The direction of the line scans is perpendicular to the direction of the line defects. The aim of the SKP measurements was not to obtain detailed information about the absolute values of the corrosion potentials at the surface of the model substrates but to obtain more insight in the relative corrosion potential distribution. Figure 5-6(a) shows a relatively constant corrosion potential for the reference model substrate surface (covered
Filiform corrosion of model substrates with synthetic chemical and topological defects

with conversion coating I) without copper-rich line defects: local variations of the corrosion potential are in the order of ~5-15 mV. The SKP line scan in Figure 5-6(b) over the model substrate with the copper-rich line defects and covered with conversion coating I shows five distinct peaks (more noble potentials) along the line scan corresponding with the position of the line defects. The potential difference between the positions of the line defects and the adjacent areas are in the order of ~100-175 mV. These variations indicate an inhomogeneous coverage of the substrate surface with the conversion coating layer I. Figure 5-6(c) shows a more constant potential distribution along the line scan with no distinct potential peaks at the position of the copper-rich line defects. This indicates a more homogeneous coverage of the substrate with the conversion coating layer II.

To understand the observed effect of the copper-rich tracks on filiform corrosion, additional experiments were performed where copper pins were inserted in holes drilled in an AA2024-T351 substrate, as illustrated in Figure 5-7. The filiform corrosion tested specimens have the following dimensions: L x L x T = 150 mm x 80 mm x 1.2 mm.

The two pretreatments applied on the samples vary from simple degreasing only, to deoxidation. It is important to note that also these pretreatments had not been optimised for maximum corrosion protection and coating adhesion, but were selected on the basis of prior industrial research practice. Prior to the surface treatment all specimens are carefully cleaned with ethanol. Degreasing included immersion for 10 minutes in Gardobond VP10036 at 60 °C, followed by a cold water rinse in running tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. The samples to be deoxidised were consequently immersed for 10 minutes in Oakite 60-FC-25 at room temperature, followed by a cold water rinse in tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. After the final step for each pretreatment the panels were air dried. Following the pretreatment, a white polyester powdercoating was deposited with an approximate post-curing coating thickness of 62 μm (standard deviation 5 μm). The same powdercoating was deposited on the reverse side of the panels. The coating was cured at 200 °C during 20 minutes. Three holes per specimen with a diameter of 5.0 mm were drilled with an intermediate distance of approximately 40 mm. The scratches were applied by scribing perpendicular to the rolling direction with a scalpel. One Cu pen per specimen was inserted in one out of the three drilled holes just before the initiation procedure, as shown in Figure 5-7. Per specimen, the filiform corrosion attack around the holes (with Cu pen and reference holes) and the scratches (with Cu pen and reference scratches) were analysed separately. The
total exposure time was 600 hours.

\[\text{Scratch through coating thickness}\]
\[l = 80 \text{ mm}\]

\[\text{AA2024-T351 base substrate}\]
\[1 \times w \times t = 150 \times 80 \times 1.2 \text{ mm}\]

**Figure 5-7:** Schematic representation of an artificially Cu-enriched AA2024-T351 model substrate

### 5.2.2 Preparation of model substrates containing magnesium defects

As illustrated in Figure 5-8, magnesium-rich tracks were ion beam implanted in commercially pure AA1060-H24 (Table 5-1). The implantation was done with the Van de Graaff accelerator of the Nuclear Solid State Physics Group of the Materials Science Centre of the University of Groningen. A chemical polishing treatment (Table 5-3) was used to provide a well-defined base substrate surface before controlled implantation. The implantations were performed using 100 keV ion beams to obtain subsurface atomic concentration levels varying from 2.5% to 5.0% and 7.5% respectively. The average depth of implantation was in the order of 200 nm. No additional mechanical or chemical treatment was applied to the surface prior to coating application. The same transparant air-drying epoxy/amine based coating as for the model substrates with copper defects was used to cover the substrates before commencing the filiform corrosion test.
Filiform corrosion of model substrates with synthetic chemical and topological defects

![Diagram](image)

**Figure 5-8:** Schematic representation of an artificially magnesium-enriched AA1060-H24 model substrate

5.2.3 Preparation of substrates with specific surface topology

The effect of rolling and grinding marks on growth direction is studied in this chapter in some detail. Furthermore, specific surface patterns have been designed with the aim of prematurely blocking filiform growth, and their effectiveness has been examined. The experimental details for this set of substrates are presented in this section. One part of the specimen surfaces were filiform corrosion tested in the as-rolled condition. A chemical polishing pretreatment (Table 5-3) was applied to the other part of AA2024-T351 specimens before they were mechanically ground and polished perpendicular to the rolling direction as shown in Figure 5-9.
Figure 5-9: Schematic representation of AA2024-T351 substrates with specific surface topology

The specimens were mechanically ground with FEPA P4000 SiC paper and consequently polished down to 3 μm. The tests were performed in duplicate. The chemical composition of the reference AA2024-T351 samples as analysed by XRF is presented in Table 5-6.

Table 5-6: XRF-analysis of the chemical composition of the base aluminium substrate AA2024-T351 in wt-%

<table>
<thead>
<tr>
<th>Element</th>
<th>AA2024-T351 as-rolled</th>
<th>AA2024-T351 chemically polished</th>
<th>AA2024-T351 chemically polished and mechanically surface treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.51</td>
<td>4.51</td>
<td>4.62</td>
</tr>
<tr>
<td>Mg</td>
<td>2.28</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>Mn</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>Fe</td>
<td>0.15</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>Si</td>
<td>0.13</td>
<td>0.08</td>
<td>0.19</td>
</tr>
<tr>
<td>Other</td>
<td>0.22</td>
<td>0.24</td>
<td>0.23</td>
</tr>
<tr>
<td>Al</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>
Filiform corrosion of model substrates with synthetic chemical and topological defects

The Mg and Si-concentrations are significantly influenced by the chemical polishing procedure, possibly by preferential dissolution of these components. The Mg-concentration is decreased from 2.28 to 1.50 wt-% after the chemical and mechanical grinding and polishing procedure. The Si-concentration decreases from 0.13 to 0.08 wt-% after the chemical procedure, and increases again to 0.19 wt-% after the mechanical surface treatments, probably related to embedding of SiC-particles in the surface layer after the grinding step. The Fe-concentration shows a more constant level of 0.14-0.16 wt-%, as well as the Mn-concentration of 0.66 wt-%. After the chemical and mechanical surface treatments the treated and reference (as rolled surfaces) samples are covered with the chromate-phosphate conversion coating I (CC-I). The presence of surface treatment marks still present after chemical polishing and mechanical surface treatment is shown by the AFM measurements in Figure 5-10. As appears from the AFM results the clear grinding and polishing marks are concealed after application of CC-I.

![AFM measurements of the AA2024-T351 surface after chemical polishing and mechanical surface treatment revealing the presence of surface treatment marks at the surface (a). The clear surface treatment mark structure seems concealed after application of CC-I (b). Scan area: 10 x 10 µm.](image)

Following the pretreatment, a clear polyester coating was applied with a wire bar and cured at a peak material temperature during 55 seconds at 240 °C. The mean dry coating thickness in this case is ~20 µm. The reverse side of the panels is protected by an air-drying polyester coating with a layer thickness of ~21 µm.
In addition to the experiments on the effects of grinding and polishing marks, also specific surface patterns have been designed with the aim of prematurely blocking filiform growth, and their effectiveness has been examined. Figure 5-11 show the surface patterns of the tested samples. Several different patterns have been applied either as single or a double blocking barrier: examples are presented in Figure 5-11(b) to (d). The patterns are applied by a scribing needle attached to an engraving unit and have a surface penetration depth of about 10 μm.

Figure 5-11: Schematic representation of an AA2024-T351 substrate with specific surface patterns (a). (b) to (d) show some examples of the surface patterns in detail

Prior to coating the samples are chromated according to the following procedure. First, degreasing by immersion for 10 minutes in Gardobond VP10036 at 60 °C, followed by a cold water rinse in running tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. Then, deoxidation by immersion for 10 minutes in Oakite 60-FC-25 at room
temperature, followed by a cold water rinse in tap water for 1 minute and a final rinse in de-ionised water for 30 seconds. Finally, application of the chromate conversion coating by immersion for 15 seconds in a ‘Alodine 1200’ solution at room temperature in accordance with product data sheets, followed by a cold water rinse in running tap water for 30 seconds and a final rinse in de-ionised water for 30 seconds. Following the pretreatment, a white polyester powdercoating was deposited with an approximate post-curing coating thickness of 62 μm (standard deviation 5 μm). The same powdercoating was deposited on the reverse side of the panels. The coating was cured at 200 °C during 20 minutes.

5.2.4 Filiform corrosion test set-up and analysis

The coating defects were applied by scribing through the organic coating, just before the initiation procedure. The filiform corrosion tests were carried out according to specification DIN65472 [5.19]. The initiation time above hydrochloric acid vapour was one hour, except for the copper pen and surface patterned samples for which an initiation time of 15 minutes was applied. The total exposure time was 1000 hours, unless reported differently in the previous sections. The degree of filiform corrosion was then determined using very accurate optical microscopy for quantifying the density and average length of the filaments. A manual procedure was used to determine the characteristic data but good care was taken in standardizing the evaluation. Both sides of the scratch were treated separately. The filiform corrosion initiation characteristics are defined as the site density which is the number of filaments per scratch length. The propagation properties are defined by the average filament length per specimen, with a resolution of 0.2-0.5 mm. The total attack is defined by the corrosion number which is equal to the site density multiplied by the average filament length.

5.3 Results and discussion

5.3.1 Filiform corrosion tests of model substrates containing copper defects

Degreased model substrates with copper-rich line defects

First, a qualitative discussion of the general appearance of the filiform corrosion progress on both reference and model substrates with copper-rich line defects is presented. The
quantification of filiform corrosion by site density, average filament length and corrosion number is presented later in this section. Figure 5-12 shows the typical filiform corrosion patterns on the degreased reference and model substrates with the artificial copper-rich line defects.

Both samples received identical thermal and surface treatments. Vertical white lines in (b) indicate the position of copper-rich artificial line defects.

**Figure 5-12:** Optical micrographs of filiform corrosion attack on reference (a) and model substrates with copper-rich line defects (b), after 1000 hours of accelerated exposure according to DIN65472 [5.19]

The filiform corrosion pattern as presented in Figure 5-12 show that filiform corrosion initiation and propagation is confined to the regions in between the copper-rich line defects on the model substrates. Furthermore, the filiform corrosion propagation rate is significantly enhanced compared to the reference substrates.
The influence of the presence of artificial copper-rich line defects on the initiation properties of the exposed substrates was examined by determining the cumulative number of initiation sites along a scratch, as shown in Figure 5-13.

*Figure 5-13: Line scan evaluation of filament initiations along a coating defect on a reference aluminium substrate and a model substrate with copper-rich line defects, after 1000 hours of accelerated exposure according to DIN65472 [5.19]. The vertical dashed lines indicate the position of the copper-rich artificial line defects.*

Also from Figure 5-13 it can be deduced that the initiation of filaments is confined to the intermediate regions for the model substrates with copper-rich line defects (horizontal plateaus are located at the position of the copper-rich lines as shown in figure 5-13). Furthermore, there is no clear trend in the position of initiation relative to the artificial copper-rich line defects. The effect on the total number and position of initiations along a coating defect is not clear due to the high site density for both substrates as shown in Figure 5-12 and to the fact that when it is taken into account that no initiations occur on the copper-rich tracks, similar site densities are calculated for both reference and the model substrates with copper-rich line defects. The site density for both the reference and the model substrates with the copper-rich line defects approximates 4.0 filaments per mm.

No clear trend of the filiform corrosion properties and the heat treatment applied was found for the model substrates tested. The average filament length values as presented in Table 5-7 represent the average values of the solution heat treated, precipitation heat treated and overaged samples. A distinction is made between the initial sputter layer thicknesses of 0 (reference), 50, 200 and 1000 nm.
Table 5-7: Average filament lengths [mm] for the degreased model substrates with copper-rich line defects. (NA: not applicable)

<table>
<thead>
<tr>
<th>Initial sputter layer thickness [nm]</th>
<th>Copper-rich defects</th>
<th>Intermediate regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (reference sample)</td>
<td>NA</td>
<td>2.33</td>
</tr>
<tr>
<td>50</td>
<td>0.00</td>
<td>3.70</td>
</tr>
<tr>
<td>200</td>
<td>0.00</td>
<td>3.63</td>
</tr>
<tr>
<td>1000</td>
<td>0.00</td>
<td>2.73</td>
</tr>
</tbody>
</table>

This quantitative analysis supports the observations that no filaments initiate at the position of the copper-rich line defects. As can be concluded from the qualitative analysis the average filament lengths in the regions in between the copper-rich line defects (2.73–3.70 mm) are (17-59%) higher than the average filament length on the reference sample (2.33 mm) after 1000 hours of accelerated exposure. This indicates that either the early initiation or the propagation of the filaments in between the copper-rich line defects is stimulated by the presence of the copper-rich noble macro defect. A high dissolution rate of the aluminium matrix in the adjacent areas, stimulated by a high cathodic reaction rate at the position of the copper-rich cathodic site, would promote filaments to either initiate at an earlier stage or propagate faster. Additional tests to discriminate between both mechanisms failed due to technical problems. As demonstrated in the previous chapter the kinetics of the cathodic reactions vary with the type of particles exposed and also their effective surface area (determined by concentration and distribution). For the present tests the exposed area is largely influenced by the initiation scribing procedure and variations in the scribing depth and therefore exposed (cathodic) surface area at the position of the line defects may occur. For this reason only trends can be expected to be observed. A further refinement of the test procedure would allow us to analyse the quantitative data in more detail. The present observations indicate that the presence of a (noble) macro defect can stimulate the filiform corrosion attack at adjacent areas relatively far away from the position of the macro defect, i.e. by a mechanism different from that proposed in earlier chapters. This effect of the presence of a (noble) macro defect at the substrate surface is investigated in more detail with filiform corrosion tests on pretreated samples and tests on AA2024-T351 with copper pens inserted in drilled holes (see later in this section).
Filiform corrosion of model substrates with synthetic chemical and topological defects

CC-I covered model substrates with copper-rich line defects

Table 5-8 shows the site density, average filament length and corrosion number for model substrates with copper-rich line defects pretreated with the chromate-phosphate based conversion coating CC-I.

Table 5-8: Site density (sd) [number of filaments per mm scratch length], average filament lengths (afl) [mm] and corrosion number (cn) for the CC-I covered model substrates with copper-rich line defects. (NA: not applicable)

<table>
<thead>
<tr>
<th>Initial sputter layer thickness [nm]</th>
<th>Copper-rich defects</th>
<th>Intermediate regions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sd</td>
<td>afl</td>
</tr>
<tr>
<td>0 (reference sample)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>50</td>
<td>0.56</td>
<td>0.33</td>
</tr>
<tr>
<td>200</td>
<td>1.42</td>
<td>0.60</td>
</tr>
<tr>
<td>1000</td>
<td>1.26</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The site density data for the CC-I covered model substrates with copper-rich line defects indicate that the number of filiform corrosion initiations is higher at the position of the copper-rich line defects than at the intermediate regions and the reference sample. The site density values in the intermediate regions and on the reference sample are comparable. Filiform corrosion initiation is not stimulated in the intermediate region for this set of samples. The site density of 0.56 for the 50 nm sample at the position of the copper-rich track is higher than for the intermediate region (0.20) and the reference sample (0.10) but relatively low compared to the values of 1.42 and 1.26 at the position of the copper-rich line defects for the 200 nm and 1000 nm samples respectively. This relatively low value can be attributed to the relatively low copper concentration at the copper-rich tracks compared to the 200 nm and the 1000 nm samples and therefore the site density is still higher but closer to the values for the intermediate regions and the reference sample. The fact that filiform corrosion initiates preferentially at the position of the copper-rich line defects is possibly to be attributed to the fact that the CC-I covers the copper-rich line defects not as well as the intermediate regions and the reference sample. The Scanning Kelvin Probe measurements presented in section 5.2.1 revealing potential peaks at the position of the copper-rich line defects after application of CC-I also indicate non-perfect
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coverage of the copper-rich line defects. For this reason the filiform corrosion may be confined to the copper-rich line defects. The absolute values of the site density, as well as the average filament length and the corrosion number at the intermediate regions and the reference sample are lower than for the degreased model substrates indicating an increased level of protection at these regions by application of CC-I.

The average filament length for the model substrates in the intermediate regions is comparable to the average filament length on the reference sample (0.25-0.33 mm). It can be concluded that the presence of the copper-rich line defect does not influence the filiform corrosion propagation in the adjacent areas. The average filament length at the position of the copper-rich line defect for the 50 nm sample is 0.33 mm and therefore comparable to that for the intermediate region and reference sample. This can possibly be attributed to the still relatively low copper concentration at the position of the line defects. For the 200 nm (0.60) and 1000 nm (0.55) samples the average filament length at the position of the copper-rich line defects is significantly higher than for the 50 nm sample and the intermediate regions and the reference sample (0.25-0.33 mm).

Analysing the total attack, defined by the corrosion number, for the present set of samples it is clear that the reference sample and the intermediate regions of the model substrates with the copper-rich line defects show similar levels of attack: corrosion numbers of 0.03–0.06 indicate a proper level of protection of these areas by the application of CC-I. At the position of the copper-rich line defects a small increase of the corrosion number is observed for the 50 nm sample (0.18) and significantly higher levels of attack are observed for the 200 nm (0.85) and 1000 nm (0.69) samples. These observations indicate the stimulating effect of the presence of copper-rich defects on the filiform corrosion characteristics within these areas. The confinement of the stimulating effect to the copper-rich line defects themselves on the initiation and propagation characteristics is related to the proper level of protection of the adjacent areas provided by the application of CC-I.

CC-II covered model substrates with copper-rich line defects

Next, we will analyse the filiform corrosion test results for the CC-II covered model substrates with copper-rich line defects. Analysis of the site density, average filament length and corrosion number shows that the reference sample and the intermediate regions of the model substrates with copper-rich line defects have similar values, as shown in Table 5-9. The filiform corrosion initiation and propagation is not stimulated in the intermediate regions. The site density, average filament length and the corrosion number
Filiform corrosion of model substrates with synthetic chemical and topological defects

show low values at the position of the copper-rich line defects. This may be related to the low chance of filiform corrosion occurrence at the position of the line defects with relatively low site densities as only a very small scratch length can be analysed for the filiform corrosion initiation and propagation at the position of the copper-rich line defects. For small site densities and small exposed scratch length the quantitative data may not be representative for the position of the copper-rich line defects. These observations indicate that the coverage of the surface by CC-II gives a good overall protection of the exposed surface. This observation is implicitly supported by the Scanning Kelvin Probe measurements presented in section 5.2.1 which did not show distinct potential peaks for the line scan across the copper-rich line defects.

Table 5-9: Site density (sd) [number of filaments per scratch length], average filament lengths (afl) [mm] and corrosion number (cn) for the CC-II covered model substrates with copper-rich line defects. (NA: not applicable; NT: not tested)

<table>
<thead>
<tr>
<th>Initial sputter layer thickness [nm]</th>
<th>Copper-rich defects</th>
<th>Intermediate regions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sd</td>
<td>afl</td>
</tr>
<tr>
<td>0 (reference sample)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>50</td>
<td>0.06</td>
<td>0.22</td>
</tr>
<tr>
<td>200</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>1000</td>
<td>NT</td>
<td>NT</td>
</tr>
</tbody>
</table>

Summarising the filiform corrosion results for the model substrates with the copper-rich line defects it can be concluded that, depending on the level of pretreatment of the substrate surface, the presence of a (noble) copper-rich macro defect can influence the filiform corrosion behaviour of the substrate surface adjacent as well as far away from the defect. This is particularly shown for the degreased only model substrates: longer filaments were observed in the intermediate regions for the model substrates with copper-rich line defects compared to the reference substrate with such synthetic copper enrichments after 1000 hours of accelerated exposure. This influencing effect of the macro defects of the adjacent areas could not be observed when this adjacent area is well protected by the presence of a chromate based conversion coating as was the case after application of CC-I and CC-II. For
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CC-I the copper-rich line defect itself was not well covered and the filiform corrosion was observed to be confined to the region of the copper-rich line defect. After application of CC-II also the copper-rich line defect was well covered and no particular stimulation of filiform corrosion initiation or propagation could be observed on these model substrates compared to the reference sample.

AA2024-T351 substrates with copper pens inserted in drilled holes
The filiform corrosion stimulating effect of the presence of a macro defect is further investigated by accelerated exposure of AA2024-T351 substrates with copper pens inserted in drilled holes. The levels of protection are kept relatively low, to prevent the stimulating effect to be masked by good protection of the surface and filiform corrosion from occurring, and vary from degreasing only to deoxidising. The quantitative analysis of the filiform corrosion pattern is done separately for the holes (with and without copper pens) and the scratches originating from these holes.

The values for the site density on these substrates is presented in Table 5-10.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Copper pen</th>
<th>Reference (no copper pen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hole</td>
<td>scratch</td>
</tr>
<tr>
<td>degreased</td>
<td>1.27</td>
<td>1.25</td>
</tr>
<tr>
<td>deoxidised</td>
<td>0.38</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Comparing the site density of the reference hole (0.32) and scratch (1.19) indicates that non-similar initiation conditions are present for the hole and the scratch configurations. The filiform corrosion characteristic values for the holes and the scratches can therefore not be compared directly. The characteristic values for the holes and scratches can be compared amongst themselves (copper pen hole with reference hole and copper pen scratch with reference scratch). Both for the degreased and the deoxidised samples it can be concluded that the filiform corrosion initiation around the copper pen hole is stimulated by the presence of such (noble) macro defect. For the degreased sample the site density of 1.27 is significantly higher than the value of 0.32 for the reference hole; for the deoxidised sample these values are 0.38 and 0.00 respectively. For the degreased sample the site density in the copper pen scratch (1.25) is not significantly higher that that for the reference...
Filiform corrosion of model substrates with synthetic chemical and topological defects

scratch (1.19) but for the deoxidised sample the value of 0.32 for the copper pen scratch is relatively high compared to that of 0.19 for the reference scratch: a relative increase of ~68%. These observations show that for the degreased samples the filiform corrosion initiation is not stimulated in the adjacent areas of the copper pen macro defect, for the deoxidised samples it is to a small extent. It is also shown that for all regions of the surface the site density for the degreased samples is significantly higher than for the deoxidised samples. The observation that deoxidising the surface reduces the susceptibility of substrate surfaces to filiform corrosion is reported earlier in literature [5.4-5.7, 5.15] and also confirmed in Chapter 6 of this thesis. The top surface layer of the tested alloys prove to be very susceptible to filiform corrosion.

The average filament length for the AA2024-T351 substrates with inserted copper pens is presented in Table 5-11.

Table 5-11: Average filament length [mm] for the AA2024-T351 substrates with inserted copper pen

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Copper pen</th>
<th>Reference (no copper pen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hole</td>
<td>scratch</td>
</tr>
<tr>
<td>degreased</td>
<td>2.93</td>
<td>1.36</td>
</tr>
<tr>
<td>deoxidised</td>
<td>2.00</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Again evaluation of the average filament length for the holes and scratches is done separately. For all tested conditions (degreased and deoxidised) and regions (holes and scratches) it is clear that the average filament length after 1000 hours of accelerated exposure is higher for the hole and scratch with the copper pen compared to the reference regions. The average filament length at the position of the hole with the copper pen (2.93 mm) is significantly higher that at the reference hole (1.40 mm) for the degreased sample. Also the presence of the copper pen stimulates the average filament length in the adjacent scratch for these samples as the average filament length for the scratch with the copper pen (1.36 mm) is higher than for the reference scratch (1.08 mm). Equivalent trends are observed for the deoxidised samples: the average filament length at the hole with the copper pen (2.00 mm) is higher than that at the reference hole where no filaments originated (0.00 mm). Also for the deoxidised samples the filiform corrosion propagation is stimulated in the scratch adjacent to the copper pen (1.69 mm) compared to the reference scratch (1.02 mm). For all regions the values of Table 5-11 show that the filiform corrosion
propagation rate is decreased by the deoxidising procedure.
The corrosion number of the tested substrates with copper pen macro defects is shown in Table 5-12.

**Table 5-12:** Corrosion number for the AA2024-T351 substrates with inserted copper pen

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Copper pen</th>
<th>Reference (no copper pen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hole</td>
<td>scratch</td>
</tr>
<tr>
<td>degreased</td>
<td>3.72</td>
<td>1.71</td>
</tr>
<tr>
<td>deoxidised</td>
<td>0.76</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The results are in line with the conclusions drawn based on the data in Tables 5-10 and 5-11.

From the filiform corrosion tests on the AA2024-T351 with the copper pen macro defects it can be concluded that the filiform corrosion initiation and propagation directly adjacent to the (noble) macro defect is stimulated. More and longer filaments are observed at the position of the copper pen macro defects. For the degreased sample, stimulation of the filiform corrosion initiation in the adjacent scratch could not be confirmed, but the deoxidised sample shows a significant relative increase of the number of filaments in the adjacent scratch. The filiform corrosion propagation in the adjacent scratch is stimulated by the presence of the nearby copper pen, which is in line with the observations for the model samples with the copper-rich line defects. It is clear that the influencing distance of the macro defect, either as a copper-rich line defect or as a copper pen, will not be infinite but is estimated to be limited to the order of about one or a few centimeters for the present sample and defect configurations. The observations show that relatively long distance effects due to the presence of noble artificial macro defects can promote filiform corrosion in a manner effectively similar to that of noble local intermetallics.

### 5.3.2 Filiform corrosion tests of model substrates containing magnesium defects

Filiform corrosion tests are also performed on model substrates with (less noble) magnesium-rich macro line defects. The analysis of the results is limited to a qualitative evaluation of the filiform corrosion tested samples. Figure 5-14 shows the typical filiform
corrosion pattern for the model substrates with magnesium-rich line defects. Unfortunately the limited amount of scratch length exposed (of both the magnesium-rich and the reference area) makes a statistical correct evaluation of the filiform corrosion attack in a quantitative sense impossible.

![Magnesium-rich defects](image)

**Figure 5-14:** Macrograph of the filiform corrosion attack a model substrate with magnesium-rich line defects, after 1000 hours of accelerated exposure according to DIN65472 [5.19]

The samples did not show a significant trend of increasing or decreasing filiform corrosion attack with increasing subsurface atomic magnesium concentration levels of 2.5, 5.0 and 7.5 % and similar levels of attack were observed. For all substrates filiform corrosion did not initiate at the position of the magnesium-rich line defects. This is in line with the local substrate attack model presented in Chapter 4. In the case of the presence of anodic phases, such as the magnesium-rich macro phases for the present set of model substrates, rapid matrix dissolution is not likely. The anodic phases will dissolve preferentially leaving behind a relatively homogeneous substrate surface. In the absence of heterogeneities in the substrate surface, localised corrosion by the formation of microgalvanic couples will not occur, leading to a relatively low substrate surface attack rate, hardly depending on the concentration of the anodic particles. In Chapter 2 it was also shown that the Al-Mg binary model substrates were the least susceptible substrates amongst the Al-Mg, Al-Zn, Al-Si and Al-Cu binary model alloys. For the adjacent areas no clear trend of the number of initiations and filiform corrosion propagation as a function of the distance from the magnesium-rich line defect could be
observed. As can be expected from theory, the anodic magnesium-rich macro defect is not likely to stimulate the filiform corrosion initiation and propagation at the adjacent areas. It is clear that compared to the model substrates with the copper-rich macro defects, opposite trends can be observed in view of the filiform corrosion attack. The presence of the (noble) cathodic copper-rich macro defects stimulated the filiform corrosion attack in the adjacent areas, by the promotion of the cathodic reduction reaction at these macro defects. In the absence of such cathodic phases, the cathodic reaction is not stimulated and the substrates prove to be much less susceptible to filiform corrosion. Active anodic phases may dissolve, leaving behind a more homogeneous aluminium rich matrix, being less susceptible to localised attack due to the lack of noble particles.

5.3.3 Filiform corrosion tests of substrates with specific topological defects

The results of an investigation into the effects of surface texture on filiform corrosion propagation for two grades of AA2024-T351 are presented in this section.

AA2024-T351 substrates with chemically polished and mechanically ground and polished surfaces

The effect of chemical polishing and subsequent mechanical grinding and polishing on the directionality and susceptibility to filiform corrosion is investigated by accelerated filiform corrosion testing. One part of the specimen surfaces were filiform corrosion tested in the as-rolled condition. A chemical polishing pretreatment was applied to the other part of AA2024-T351 specimens before they were mechanically ground and polished perpendicular to the rolling direction.

First, a qualitative discussion of the general appearance of the filiform corrosion progress on both as-rolled and surface treated substrates is presented. Figure 5-15 shows the typical filiform corrosion patterns on the as-rolled and surface treated AA2024-T351 substrates.
Figure 5-15: Macrograph of the filiform corrosion attack on as-rolled ((a) to (c)) and surface treated ((d) to (f)) AA2024-T351, after 48 hours (a) and (d), 400 hours (b) and (e) and 1000 hours (c) and (f) of accelerated exposure according to DIN65472 [5.19]

This Figure 5-15 shows that the filiform corrosion propagation direction for the as-rolled surfaces is preferentially in the rolling direction. For the surface treated (perpendicular to the rolling direction) substrate the preferential filiform corrosion propagation direction is in the direction of the mechanical grinding and polishing, perpendicular to the original rolling direction. It is reported in the literature that filaments typically follow the rolling direction [5.3, 5.4, 5.6, 5.7, 5.15, 5.16] or scratch lines on a ground surface [5.3, 5.4, 5.17] which is in line with the present observations. The grinding or working of the substrate surface can have an indirect chemical effect, but the surface topology determined guidance of the growth direction can also be just geometrical. The chemical effect of rolling, grinding and working is attributed to the alignment of particles (i.e. precipitates, dispersoids and constituent particles) in the direction of rolling, grinding or working [5.20, 5.21]. The effect of the concentration of cathodic or anodic particles and their distribution is discussed.
in Chapter 4. For a high concentration and/or fine distribution of particles it is likely that other ‘fresh’ cathodic particles are more rapidly reached by the corroded zone around active particles, which in turn will participate in the substrate matrix dissolution. By rolling, grinding or working, particles are broken up and redistributed, preferentially as strings of particles in the direction of the mechanical surface treatment process [5.20, 5.21]. Consequently, a higher concentration and/or finer distribution of particles will be present in this direction, as schematically shown in Figure 5-16. The increased cathodic area will therefore lead to rapid spread of the corrosion front in this direction and thus a high filiform corrosion propagation rate relative to the other directions.

![Diagram](image)

**Figure 5-16**: Schematic representation of the indirect chemical effect of rolling, grinding and working on the preferential filiform corrosion propagation direction

The geometrical effect of rolling, grinding and working can be explained best with the aid of Figure 5-17.

When analysing the longitudinal section in Figure 5-17(b) it can be seen that the (schematic) incident angle of the very tip of the filament is relatively small compared to the angle of incidence for the situation (angle of incidence on Face I) represented in the cross-sectional view of Figure 5-17(c). For surface faces with the orientation according to Face I it can be seen that the angle between the filament tip front and the substrate surface can represented by a relatively blunt notch, while the notch for the longitudinal section is relatively sharp and constant. From classical crack tip propagation theory it can be assumed that, assuming similar chemical substrate surface conditions and mechanical pressure in the filament tip in all directions, the ‘crack tip’, in this case the filament tip, is likely to open and propagate in the direction of the sharp notch (small angle of incidence) and thus in the direction of rolling, grinding or working.
Figure 5-17: Schematic representation of an AA2024-T351 substrate with specific surface patterns. (a) shows a top view of a filament on a rolled/ground surface. (b) and (c) are schematic representations of a longitudinal and cross-sectional view of the filament tip on the trenched surface respectively.

In practice, surfaces are not ideally perfect and surface textures different from those represented in Figure 5-17 can be encountered. For this reason occasionally also propagation directions different from the rolling, grinding and working direction can be observed as shown in Figure 5-15. In general these deflections from the preferential direction are characterised by discrete steps and the propagation direction after the deflection usually is in rolling, grinding or working direction again. These discrete steps can be caused by discrete substrate surface imperfections and also a sudden and discrete propagation direction change can be encountered when the angle of incidence as shown in Figure 5-17(c) is on faces with orientations according to Face II. In these cases a very low angle of incidence and thus a sharp notch can cause discrete propagation direction changes opposite or perpendicular to the rolling, grinding or working direction. Gradual and steady propagation of filaments in directions other than the rolling, grinding or working direction is seldomly observed. The theory of the geometrical effect on preferential propagation direction is implicitly supported by observations in the literature if a pronounced topography is removed either by very fine mechanical polishing, etching, anodising or sandblasting [5.3, 5.4, 5.6], the directionality is lost and a more random filiform corrosion growth direction takes over.

The relative contributions of the chemical effect on one hand and geometrical effects on the other hand of rolling, grinding and working on the preferential filiform corrosion propagation direction is not established unambiguously yet.

Quantitative analysis of the results is presented in Figure 5-18. Site density, average
filament length and the corrosion number are analysed separately. These values are determined after 168, 500 and 1000 hours of accelerated exposure respectively.

**Figure 5-18:** Site density (a) [number of filaments per scratch length], average filament lengths (b) [mm] and corrosion number (c) for the as rolled and surface treated AA2024-T351 substrates

The values for the site density in Figure 5-18(a) show that after 1000 hours of accelerated exposure the number of initiations along the scratch is relatively independent of the substrate surface condition, either rolled (1.13) or surface treated (1.20). However, the initiation rate for the surface treated samples is relatively high compared to that for the as
rolled surfaces: after 168 hours the site density for the surface treated samples is 1.04 while for the as rolled surfaces a site density of 0.80 is reached at that point. Figure 5-18(a) also shows that virtually all filaments originated in the first half (500 hours) of the total exposure time for both the as rolled (~97%) and the surface treated (~99%) surfaces. After 168 hours also most of the total number of filaments have initiated for both the as rolled (~71%) and surface treated (~87%) surfaces. It can be concluded that the filiform corrosion initiation rate decreases with time for the substrates tested.

When analysing the average filament length for the substrates tested it can be seen that after all exposure times the average filament length for the surface treated samples is higher than for the as rolled surfaces. After 1000 hours of exposure the average filament length for the as rolled surfaces (1.22 mm) is ~74% of that for the surface treated samples (1.65 mm). It is reported that mechanical grinding of aluminium surfaces prior to coating give no improvement of the filiform corrosion susceptibility compared to degreasing [5.3, 5.4, 5.15, 5.17, 5.18]. It is even reported that dry sanding of aluminium alloy surfaces increased the filiform corrosion susceptibility significantly, attributed to the presence of embedded impurities at the substrate surface after sanding [5.14]. This embedding of impurities after the mechanical grinding and polishing procedures, such as SiC, is also observed for the present set of alloys as discussed in section 5.2.3. Figure 5-16(b) also shows a decreasing propagation rate with time. After 17% (168 hours) and 50% (500 hours) of the total exposure time (1000 hours), 31/36% and 82/79% of the average filament length (1.22/1.65 mm: 100/100%) after 1000 hours of exposure for the as rolled/surface treated surfaces is observed.

The corrosion number after 1000 hours of accelerated exposure for the surface treated samples (1.98) is significantly higher than for the as rolled surfaces (1.38). For all exposure times this higher corrosion number is mainly caused by the higher average filament length for the surface treated samples as explained earlier in this section. For the shorter exposure time of 168 hours also the higher filament initiation rate of the surface treated samples adds to this observation of a higher corrosion number.

**AA2024-T351 substrates with specific surface patterns**

In this part the qualitative observations of the filiform corrosion tested AA2024-T351 samples with specific surface patterns are presented. Figure 5-19 shows the relative effectiveness and influencing effect of the presence of specific surface patterns on the filiform corrosion propagation.
Figure 5-19: Optical micrographs of filiform corrosion tested AA2024-T351 substrates with specific surface patterns. (a) to (c) show the filiform corrosion attack for the patterned surfaces, (d) shows the reference sample without the specific surface patterns.

Figure 5-19(a) shows the deflection of a filament at the position of a line shaped scribe into the substrate surface underneath the organic coating. As explained for the rolling, grinding or working marks in this section from a geometrical point of view, the filament is also less likely to cross such relatively deep and discrete surface mark and will preferentially deflect over the relatively less pronounced rolling marks. Also Figures 5-19(b) and (c) show the effectiveness of the surface patterning in confining the filiform corrosion in between the coating defect and the surface marks. The relative blocking performance of the AA2024-T351 samples with different barrier configurations was found to be at similar levels: no
specific preferable surface pattern for blocking filiform corrosion propagation could be deduced from the present set of samples. The reference samples do not show restricted or confined filiform corrosion propagation by the absence of the surface marks as shown in Figure 5-19(d).

5.4 Conclusions

The present investigation shows the possibility of stimulation of filiform corrosion on exposed surfaces by the presence of nearby (noble) macro defects. From the filiform corrosion tests on the AA2024-T351 with the inserted copper pen it can be concluded that the filiform corrosion initiation and propagation directly adjacent to the (noble) macro defect is stimulated. More and longer filaments are observed at the position of the copper pen macro defects. For the degreased sample, stimulation of the filiform corrosion initiation in the adjacent scratch could not be confirmed, but the deoxidised sample shows a small absolute but significant relative increase of the number of filaments in the adjacent scratch. The filiform corrosion propagation in the adjacent scratch is stimulated by the presence of the nearby copper pen in all cases, which is in line with the observations for the degreased model samples with the copper-rich line defects. The, least protected, degreased samples with the copper-rich line defect show a significant stimulation of the filiform corrosion propagation in the regions in between the copper-rich line defects. It is clear that the influencing distance of the macro defect, either as a copper-rich line defect or as a copper pen, will not be infinite but is estimated to be limited to the order of about one or a few centimeters for the present sample and macro defect configurations. The observations show that relatively long distance effects due to the presence of noble artificial macro defects can promote filiform corrosion in a manner effectively similar to that of noble local intermetallics, as discussed in the previous chapters.

For the degreased model substrates with magnesium-rich line defects, filiform corrosion did not initiate at the position of the magnesium-rich line defects irrespective of the subsurface magnesium concentration. This is also in line with the local substrate attack model presented in Chapter 4. In the case of the presence of anodic phases, such as the magnesium-rich macro phases for the present set of model substrates, rapid matrix dissolution is not likely. The anodic phases will dissolve preferentially leaving behind a
relatively homogeneous substrate surface. In the absence of noble heterogeneities in the substrate surface, localised corrosion by the formation of microgalvanic couples will not occur, leading to a relatively low substrate surface attack rate, also not very much depending on the concentration of the anodic particles.

The present investigation on surface treated AA2024-T351 samples shows that the filiform corrosion propagation direction for the as rolled surfaces is preferentially in the rolling direction. For the surface treated substrate the preferential filiform corrosion propagation direction is in the direction of the mechanical grinding and polishing, perpendicular to the original rolling direction. Both a chemistry and geometry based mechanism is discussed in this chapter to explain the preferential propagation direction. Their relative contributions are still subject of discussion.

Application of specific surface patterns on AA2024-T351 substrates is shown to be a very effective way of confining and restricting filiform corrosion attack within the set boundaries of the surface pattern.

References


5.4 K. SCHECK, PhD-Thesis, Institut für Technische Chemie der Universität Stuttgart, Germany (1991)


5.6 H. LETH-OLSEN, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1996)

5.7 A. AFSETH, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology, Norway (1999)

5.8 H. LETH-OLSEN and K. NISANCIOGLU, Corrosion 53 (1997) p. 705
5.15 W.H. SLABAUGH, W. DEJAGER, S.E. HOOVER and L.L. HUTCHINSON, J. of Paint Techn. 44 (1972) p. 76
5.19 Deutsches Institut Für Normung e.V., Number 65472: Filiform corrosion test of coatings on aluminium alloys, draft (1989)
5.21 M. ZAMIN, Corrosion 37 (1981) p. 627
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6005A and AA6063 alloys

This chapter deals with the effect of heat treatments, either before or after extrusion, on the filiform corrosion properties of two different AA6000 series alloys. To this aim, in total 20 hot top cast AA6005A and AA6063 billets (10 of each alloy), 65 cm long with a diameter of 20 cm, were extruded, in duplicate per alloy condition, on an industrial press. The extrudates were tested on their filiform corrosion properties by accelerated exposure tests.

6.1 Introduction

Aim of the present investigation is the determination of the combined effect of a heat treatment before and after the extrusion on the filiform corrosion properties of AA6005A and AA6063 and the surface pretreatment before application of the organic coating. The composition, morphology and distribution of the constituent particles in AA6005A and
AA6063 are a function of the thermomechanical treatments during the preceding production steps such as casting, solidification, homogenisation, extrusion and precipitation. The mechanical properties during and after processing of AlMgSi extrusion alloys are strongly influenced by the state of the primary alloying elements Mg and Si in the alloy. A high content of solute Mg and Si in the aluminium matrix increases the solution hardening and extrusion pressure required, but also the mechanical properties of the extrudate: it gives a high hardening potential, which is directly related to the solute concentration available for the formation of hardening β""-precipitates during artificial ageing of the alloy. On the other hand, the presence of large Mg2Si particles would reduce the extrusion pressure needed, but might cause surface cracking during extrusion and a deterioration of the hardening potential, because these particles tie up solute. The most desirable condition from an extrusion point of view would probably be an intermediate structure with small enough Mg2Si precipitates, preventing surface defects, but increasing the obtainable production speed because of the reduction of solution hardening. These particles may dissolve during extrusion and the hardening potential of the alloy will be as high as that of solutionised material.

In this study a systematic investigation has been exerted to investigate the effect of pre-extrusion heat treatments on the filiform corrosion properties of the extrudate. To this aim, two commercial AlMgSi alloys were heat treated in five different ways to create billets with one of a variety of Mg2Si particle distributions. Additionally, the filiform corrosion properties of a selection of extrudates with a complementary post-extrusion heat treatment are investigated.

An examination of the effect of these pre-extrusion heat treatment on the industrial extrusion process parameters such as extrusion pressure, speed and temperature as well as the mechanical properties of the extrudates is presented in [6.1].

Proper surface pretreatment of aluminium alloys can improve the filiform corrosion properties of aluminium alloys significantly [6.2-6.10]. For the present set of experiments the pretreatments vary from controlled degreasing via deoxidisation to the application of a chromate or cerium oxide conversion coating.

While the detailed examination of the filiform corrosion rate as a function of the heat treatment applied yields valuable results, further insight in the underlying mechanism can be obtained by performing electrochemical measurements, as shown in Chapter 3 for the binary Al-Cu and Al-Zn model alloys. To this aim potentiodynamic polarisation measurements are performed on the post-extrusion heat treated samples in synthetic
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6xxx

anolyte and catholyte media, which are characteristic for the local anodic and cathodic sites in the filaments on the aluminium.

6.2 Experimental

In this paragraph the base material details, including the applied heat treatments, the extrusion process, the surface pretreatment and application of the organic coating, the filiform corrosion test procedure as well as the experimental details for the potentiodynamic polarisation tests are presented.

6.2.1 Base material

One AA6005A and one AA6063 alloy with alloying element concentrations specified in Table 6.1 were hot top DC cast under industrial conditions to yield 10 billets each with a diameter of 20 cm and a cut-off length of 70 cm.

Table 6-1: Chemical composition of the AA6005A and AA6063 alloys [wt-%]

<table>
<thead>
<tr>
<th>Element</th>
<th>AA6005A</th>
<th>AA6063</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.69</td>
<td>0.48</td>
</tr>
<tr>
<td>Si</td>
<td>0.88</td>
<td>0.36</td>
</tr>
<tr>
<td>Fe</td>
<td>0.29</td>
<td>0.23</td>
</tr>
<tr>
<td>Mn</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>Other</td>
<td>&lt;0.08</td>
<td>&lt;0.11</td>
</tr>
<tr>
<td>Al</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

6.2.2 Pre-extrusion heat treatment

The billets were homogenised at 565 ± 20°C during 6 hours in a hot air furnace, followed by a water quench in a 180 dm³ water bath of approximately 17 ± 3°C. Of each alloy, two billets were kept in the homogenised and quenched condition, and 8 billets were pre-aged
for 24 hours at a specific temperature, followed by a water quench (two billets at each temperature), to create β' or β-type Mg2Si precipitates. These pre-extrusion heat treatments were coded WQ, β', β(1), β(2) and β(3). The detailed thermal histories are summarised in Table 6-2.

**Table 6-2:** Pre-extrusion heat treatments of the AA6005A and AA6063, together with the specific type of Mg2Si phase created

<table>
<thead>
<tr>
<th>Pre-extrusion heat treatment</th>
<th>Pre-extrusion heat treatment temperature (°C) – time (hr)</th>
<th>Precipitate type and distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>WQ</td>
<td>-</td>
<td>WQ (I)</td>
</tr>
<tr>
<td>β'</td>
<td>250 – 24</td>
<td>β'</td>
</tr>
<tr>
<td>β(1)</td>
<td>325 - 24</td>
<td>β, fine particle distribution</td>
</tr>
<tr>
<td>β(2)</td>
<td>400 – 24</td>
<td>β, intermediate distribution</td>
</tr>
<tr>
<td>β(3)</td>
<td>450 - 24</td>
<td>β, coarse particle distribution</td>
</tr>
</tbody>
</table>

The pre-ageing temperatures at 325°C, 400°C and 450°C all induce β-type Mg2Si precipitates, but with distributions differing in number of particles, morphology and volume fraction.

The heat treated billets were then sawn to a length of 65 cm for the extrusion experiments. The remaining slices were used for microstructural characterisation with Differential Scanning Calorimetry experiments [6.1] and further microscopical analysis.

**6.2.3 Extrusion process**

The billets were extruded in duplicate per alloy condition on an industrial press to a profile with cross-section as schematically shown in Figure 6-1, at temperatures and speeds typical for AA6000-series.
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6xxx

Figure 6-1: Schematic representation of the extruded profile. The bottom plane of the tapered section (T = 4-2.5 mm) on the right hand side of this profile is used for the filiform corrosion tests.

Before extrusion the billets were pre-heated in an induction furnace to 480°C within 20 minutes, then they were placed in the billet container and immediately extruded at constant ram speed. After extrusion the extrudate was cooled with forced air. Extrusion process parameters such as extrusion pressure, speed and temperature were recorded and the mechanical properties as function of annealing treatment were determined after the extrusion and are presented in further detail in [6.1]. During the extrusion of AA6005A in the β(1) condition die breakdown occurred [6.1]. For this reason only the β' and β(1) pre-extrusion heat treated conditions of the AA6005A could be evaluated on their filiform corrosion properties. For the AA6063 all five conditions could be tested.
6.2.4 Post-extrusion heat treatment

On one of the pre-extrusion heat treated AA6063 extrudates an additional post-extrusion heat treatment series has been applied before the filiform corrosion tests were started. This alloy condition is the AA6063-WQ condition (pre-extrusion heat treatment: solution heat treatment at 565 °C for 6 hours, followed by water quenching). The seven different post-extrusion heat treatment procedures are listed in Table 6-3. As a reference and as a check for the reproducibility of the test conditions a second set of the only pre-extrusion homogenised AA6063-WQ has also been tested in this second series of post-extrusion heat treated samples.

Table 6-3: Post-extrusion heat treatments of the AA6063-WQ extrudate, together with the specific type of Mg2Si phase created

<table>
<thead>
<tr>
<th>Pre-extrusion condition</th>
<th>Post-extrusion heat treatment temperature (°C) – time (hr)</th>
<th>Post-extrusion condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>WQ</td>
<td>-</td>
<td>WQ (II)</td>
</tr>
<tr>
<td>185 – 6</td>
<td>WQ - T6 temper</td>
<td>WQ - β'</td>
</tr>
<tr>
<td>250 – 24</td>
<td>WQ - β(1)</td>
<td>WQ - β(2)</td>
</tr>
<tr>
<td>325 – 24</td>
<td>WQ - β(1)</td>
<td>WQ - β(3)</td>
</tr>
<tr>
<td>400 – 24</td>
<td>WQ - WQ</td>
<td>WQ - WQ + β(3)</td>
</tr>
<tr>
<td>450 – 24</td>
<td>WQ - WQ</td>
<td></td>
</tr>
<tr>
<td>565 – 6</td>
<td>WQ - WQ</td>
<td></td>
</tr>
<tr>
<td>565 – 6 + 450 – 24</td>
<td>WQ - WQ + β(3)</td>
<td></td>
</tr>
</tbody>
</table>

6.2.5 Filiform corrosion tests

The filiform corrosion tested specimens are ribbon-sawn out of the extrudate to the following dimensions: L x LT x T= 150 mm x 75 mm x 4-2.5 mm. Two sets of filiform corrosion tests are performed according to the DIN65472 specification [6.11]: the pre- and post-extrusion heat treated samples are tested separately in two subsequent exposure runs under the same nominal test conditions.

The four pretreatments applied on both series of samples vary from simple degreasing, to
deoxidation, chromating or cerating. It is important to note that none of the conditions of application of these pretreatments had been optimised for maximum corrosion protection and coating adhesion before the study commenced, but conditions were selected on basis of earlier experiences. Prior to the surface treatment all specimens are carefully cleaned with ethanol.

Degreasing
Immersion for 10 minutes in Gardobond VP10036 at 60 °C, followed by a cold water rinse in running tap water for 1 minute and a final rinse in de-ionised water for 30 seconds.

Deoxidation
- Degreasing in Gardobond VP10036, as above.
- Deoxidation by immersion for 10 minutes in Oakite 60-FC-25 at room temperature, followed by a cold water rinse in tap water for 1 minute and a final rinse in de-ionised water for 30 seconds.

Chromate Conversion Coating
- Degreasing in Gardobond VP10036, as above.
- Deoxidation in Oakite 60-FC-25, as above.
- Chromate conversion coating by immersion for 15 seconds in a ‘Alodine 1200’ solution at room temperature in accordance with product data sheets, followed by a cold water rinse in running tap water for 30 seconds and a final rinse in de-ionised water for 30 seconds.

Cerate Conversion Coating [6.12]
- Degreasing and deoxidation as above for chromate conversion coating.
- Cerating at 45°C by immersion for 5 minutes, followed by cold water rinse in running tap water for 30 seconds and a final rinse in de-ionised water for 30 seconds.

After the final step for each pretreatment the panels were air dried. Following the pretreatment, a white polyester powder coating was deposited with an average post-curing coating thickness of 62 μm (standard deviation 5 μm). The same powder coating was deposited on the reverse side of the panels. The coating was cured at 200 °C during 20 minutes. The coating defect was applied by scribing perpendicular to the rolling direction.
with a scalpel, just before the initiation procedure. Per alloy condition one specimen has been evaluated (one specimen per set of two extruded billets). Per specimen investigated, three scribes with an individual length of 60 mm and intermediate spacing of 42 mm were applied. Consequently a total scratch length of 180 mm was examined. Both sides of the scratches were analysed separately. The total exposure time was 1000 hours. The degree of filiform corrosion was determined using optical microscopy for quantifying the filiform corrosion attack. A manual procedure was used to determine the characteristic data but good care was taken in standardizing the evaluation. The filiform corrosion initiation characteristics are defined as the site density, which is the number of filaments per scratch length. The propagation properties are defined by the average filament length per specimen, with a resolution of 0.5 mm. The total attack is quantified by a so-called corrosion number, which is equal to the site density multiplied by the average filament length.

6.2.6 Potentiodynamic polarisation measurements

In this section experimental details of the potentiodynamic polarisation measurements are presented briefly. More detailed information about the theoretical background and experimental part of the combined filiform corrosion and potentiodynamic polarisation tests is discussed extensively in Chapter 3, sections 3.2 and 3.3.

Potentiodynamic polarisation measurements are performed on the post-extrusion heat treated samples, with alloy codes as listed in Table 6-4, in synthetic anolyte and catholyte media, which are characteristic for the local anodic and cathodic sites in the filaments on the aluminium. The potentiodynamic polarisation measurements typical for the anodic site are performed in the following anolyte: 0.86 M NaCl + 0.1 M AlCl₃, acidified to pH 2 with concentrated HCl (33%) and actively deaerated with high purity nitrogen gas. The polarisation measurements in the catholyte are conducted in a solution of distilled water adjusted to pH 10 by addition of NaOH and actively aerated with air. The electrochemical cell consisted of an Avesta cell, the aluminium based alloy as a working electrode (working area 0.8 cm²), a commercial saturated calomel reference electrode (SCE) and a platinum cylindrical small-mesh wire netting counter electrode. Prior to the electrochemical measurements the specimens are degreased with ethanol. The open circuit potential (OCP) of the system was allowed to become stationary over a 5 hour period before the commencement of the polarisation scans. Even though some corrosion did occur during this period, the time at the OCP prior to testing did ensure that the system was stable,
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enabling proper potentiodynamic polarisation measurements at a stable OCP on a surface representative of an active anodic or cathodic site in a filament. The scan rate for the potentiodynamic polarisation experiments was 0.2 mV/sec. The scans in the anolyte were started at −200 mV vs. OCP to +200 mV vs. OCP; in the catholyte the scans were started at +50 mV vs. OCP to −500 mV vs. OCP. The potentiodynamic polarisation scans were carried out at room temperature using a PAR273A potentiostat.

Table 6-4: The alloy codes of the post-extrusion heat treated samples for the potentiodynamic polarisation tests

<table>
<thead>
<tr>
<th>Pre-extrusion condition</th>
<th>Post-extrusion heat treatment temperature (°C) – time (hr)</th>
<th>Alloy code</th>
</tr>
</thead>
<tbody>
<tr>
<td>WQ</td>
<td>-</td>
<td>AE</td>
</tr>
<tr>
<td></td>
<td>185 – 6</td>
<td>T6</td>
</tr>
<tr>
<td></td>
<td>250 – 24</td>
<td>β'</td>
</tr>
<tr>
<td></td>
<td>325 – 24</td>
<td>β(1)</td>
</tr>
<tr>
<td></td>
<td>400 – 24</td>
<td>β(2)</td>
</tr>
<tr>
<td></td>
<td>450 – 24</td>
<td>β(3)</td>
</tr>
</tbody>
</table>

6.3 Results

In this paragraph the microscopical analysis of the pre- and post-extrusion conditions and the filiform corrosion morphology and quantitative characteristics are discussed.

6.3.1 Microscopical analysis of alloy conditions

Pre-extrusion analysis

Some of the typical optical micrographs of the pre-extrusion microstructures of the AA6005A billets in the WQ, β(1), β(2) and β(3) conditions are shown in Figure 6-2, revealing the most relevant microstructural changes after heat treatment before extrusion of AlMgSi alloys.
Figure 6-2: Optical micrographs of the AA6005A billets in different pre-extrusion heat treatment conditions: WQ (a), β(1)(b), β(2) (c) and β(3) (d)

Figure 6-2(a) through (d) all show large strings of constituent particles on the grain boundaries. EDX analysis of these grain boundary particles indicate the presence of Al, Fe, Mn and Si. Comparing Figure 6-2(a) to 6-2(d) shows that smaller particles can be observed in between the Al, Fe, Mn and Si containing particles: these particles are β-Mg2Si particles. The distribution of these Mg2Si-particles coarsens with increasing pre-extrusion heat treatment temperature: their distribution in the grain interior is much finer in the WQ condition compared to that in the β(3) condition. The largest Mg2Si-particles are ~1 μm in size. Also, e.g. Figure 6-2(d) shows that in between, and possibly on, the Al, Fe, Mn and Si containing particles smaller, dark or transparent β-particles appear. The micrographs of the AA6063 alloy showed similar trends, but with somewhat smaller particles and lower particle densities. The micrographs of the β'-condition were similar to those of the WQ condition. These observations are in line with results from the DSC-measurements [6.1]

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showing the precipitation behaviour and coarsening of particles sizes (and herewith coarsening of the particles distribution) with increasing pre-extrusion heat treatment temperatures. It is concluded that the pre-extrusion heat treatments have led to the intended conditions of Mg and Si, mentioned in Table 6-2.

Post-extrusion analysis

Figure 6-3 shows the relevant effects of post-extrusion heat treatment on the microstructures of extruded AA6005A and AA6063.

![Microstructures of extruded AA6005A and AA6063](Image)

Figure 6-3: Optical micrographs of post-extrusion heat treated AA6005A and AA6063 extrudates. (a) and (b) show the microstructures in the AA6063-WQ and AA6063-β(3) condition, (c) and (d) are the AA6063 and the AA6005A in the β' condition respectively.
Figure 6-3(a) through (d) show that the Al, Fe, Mn and Si containing constituent particles are also clearly present in the extruded alloy, but the strings have broken up, giving a more random distribution of constituent phases through the alloy. Figure 6-3(a) through (c) indicate for the AA6063 alloy that most of the darker and transparent particles have disappeared and the differences between the differently heat treated samples is negligible. This indicates that most Mg$_2$Si phases created prior to extrusion by the pre-extrusion heat treatment have dissolved during hot extrusion. Comparing Figure 6-3(c) and (d) shows that the specimen AA6005A contains more (relatively small) intermetallic particles than the AA6063, correlating to the higher Mg and Si concentration for the AA6005A alloy.

6.3.2 Filiform corrosion morphology

Before a quantitative analysis of the filiform corrosion characteristics is presented, first a qualitative analysis of the filiform corrosion attack morphology is given. In Chapter 3 a more detailed discussion on the attack morphology as revealed by coating removal is presented. In this paragraph only the general filiform corrosion appearance for this set of tested alloys is given with variation of the surface pretreatment. The filiform corrosion attack morphology appears independent of the alloy condition. In contrast, the filiform corrosion attack morphology varies with the surface pretreatment applied.

Figures 6-4(a) and 6(b) are optical macrographs from the same attacked area on the as degreased tested AA6063-WQ sample, but taken with different optical techniques. Figure 6-4(a), as well as Figure 6(c) through 6-4(e), is taken with a low angle of incidence light microscopy technique whereas Figure 6-4(b) is taken with the Nomarski interference contrast technique. Due to the very flat filiform corrosion propagation on the degreased only surfaces very little elevation of the organic coating is observed by inclined field lighting and this smoother filiform corrosion morphology is better observed with the interference contrast technique. The other three pretreatments resulted in a more rugged and pronounced filiform corrosion morphology with more elevated filament contours. Besides being flatter, the filaments on the degreased only samples are longer and wider than the filaments on the other pretreated samples. The differences in filament height and width between the degreased samples on the one hand and the deoxidised, chromated and cerated ones on the other hand are due to differences in the adhesion strength between the organic coating and the substrate surface.
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6xxx

Figure 6-4: Optical macrographs of the filiform corrosion morphology on AA6063-WQ, with variation of the surface pretreatment ranging from degreasing only, (a) and (b), to deoxidising (c), chromating (d) and cerating (e).
For a relatively low adhesion strength (degreased samples) the filament volume increase by the build-up of corrosion product is accommodated by delamination of the organic coating at the edges of the filament preferred to stretching of the organic coating. This results in relatively flat and wide filaments. For higher adhesion strengths (deoxidised, chromated and cerated samples), the filament volume increase is accommodated by coating stretching preferred to coating delamination, resulting in relatively narrow and high filaments. The typical filament widths for the as degreased samples is 0.8-1.0 mm whereas for the other pretreatments the filament widths are 0.2-0.5 mm typically. The average filament lengths of all samples are summarised in the next paragraph.

Besides the individual average filament lengths, the exact data for the site density and resulting corrosion number are presented in the next paragraph. On the deoxidised, chromated and cerated surfaces the filaments showed a recurrent necking or closely packed blister propagation pattern along the filament tail. This pattern is less clear for the degreased only samples due to the smoother filiform corrosion attack morphology. The observation of recurrent necking supports an apparent stepwise filiform propagation [6.13, 6.14].

6.3.3 Site density

Pre-extrusion heat treatment

In Table 6-5 the filament site densities for all AA6005A and AA6063 samples are presented. A maximum site density of 0.78 filaments per mm scratch length is obtained for the deoxidised AA6063-β' sample and a minimum site density of 0.27 for the degreased AA6005-β' condition.

The degreased test series show the highest filament density in the β' and β(1) conditions with site densities of 0.66 and 0.67 respectively compared to 0.51, 0.54 and 0.55 for the WQ(I), β(2) and β(3) conditions respectively. Consequently, the maximum site density / minimum site density ratio (max/min sdr), indicating the relative microstructural effect for a specific pretreatment, for the degreased samples is 1.31. Based on overall results, the ratio of max/min sdr for a set of five identical samples is estimated to be less than 1.20. Hence, the results indicate real microstructural effects.

For the deoxidised test series the maximum site density is obtained for the β' condition and a general trend of decreasing site density with coarser precipitate distribution, with the site density for the WQ (I) condition comparable with the β(1) condition. The max/min sdr for
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the deoxidised samples is 1.59.

The same trend applies to the chromated test series with a maximum site density for the $\beta'$ condition of 0.64 and a minimum site density of 0.41 for the $\beta(3)$ condition. The max/min sdr for the chromated samples is 1.56.

**Table 6-5:** Site density [filaments per mm scratch length] of pre-extrusion heat treated AA6005A and AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-2 and average sd and max/min sdr are defined in the text)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (1)</td>
<td>0.51</td>
<td>0.61</td>
<td>0.51</td>
<td>0.64</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>0.66</td>
<td>0.78</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>$\beta(1)$</td>
<td>0.67</td>
<td>0.61</td>
<td>0.55</td>
<td>0.63</td>
</tr>
<tr>
<td>$\beta(2)$</td>
<td>0.54</td>
<td>0.49</td>
<td>0.55</td>
<td>0.67</td>
</tr>
<tr>
<td>$\beta(3)$</td>
<td>0.55</td>
<td>0.54</td>
<td>0.41</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>Average sd</strong></td>
<td>0.59</td>
<td>0.61</td>
<td>0.53</td>
<td>0.64</td>
</tr>
<tr>
<td><strong>Max/min sdr</strong></td>
<td><strong>1.31</strong></td>
<td><strong>1.59</strong></td>
<td><strong>1.56</strong></td>
<td><strong>1.12</strong></td>
</tr>
<tr>
<td>AA6005A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta'$</td>
<td>0.27</td>
<td>0.67</td>
<td>0.65</td>
<td>0.77</td>
</tr>
<tr>
<td>$\beta(1)$</td>
<td>0.44</td>
<td>0.72</td>
<td>0.52</td>
<td>0.72</td>
</tr>
</tbody>
</table>

For the cerated samples the microstructural variation effects on the site density parameter are levelled off: with a maximum site density of 0.67 in the $\beta(2)$ condition and a minimum site density of 0.60 for the $\beta(3)$ condition the max/min sdr, indicating the relative microstructural effect, is only 1.12. Based on the estimated max/min sdr value of 1.20 for five identical samples, it can be concluded that the value of 1.12 does not represent real microstructural effects.

From these results it can be concluded that the relative microstructural effect, characterised by the max/min sdr, after pre-extrusion heat treatments are the largest for the deoxidised
and chromated test samples and this sensitivity decreases significantly for the degreased and is essentially masked by the cerate treatment. Following the discussion in subparagraph 6.3.1, showing little microstructural differences for the different pre-extrusion heat treatments, it can be concluded that in spite of the limited range of these differences, they can influence the filiform corrosion initiation characteristics to some extent, depending on the surface pretreatment. The present observations confirm an increasing filiform corrosion initiation sensitivity with a finer precipitate distribution, however the microstructural analysis presented in section 6.3.1 indicates only small microstructural differences for the extrudates after pre-extrusion heat treatment. For the AA6063 series the average site density is the lowest for the chromated samples (0.53) whereas the degreased (0.59), deoxidised (0.61) and the cerated (0.64) test series only show minor differences. The application of the chromate conversion coating proves to be the most effective way to minimise the filiform corrosion initiation characteristics.

The AA6005A test series do not give clear and consistent results for the different pretreatments. The site density for the degreased only samples show very low site densities of 0.27 and 0.44 for the $\beta'$ and $\beta(1)$ condition respectively. For the deoxidised and cerated test series these are much higher but similar for both alloy conditions, varying only between 0.67 for the deoxidised $\beta'$ condition and 0.77 for the cerated $\beta'$ condition. The chromated AA6005A conditions are somewhat lower, 0.65 and 0.52 for the $\beta'$ and $\beta(1)$ condition respectively. As yet, especially the very low site density values for the degreased only AA6005A are unclear and possibly related to specific physical surface effects as the profiles were extruded with a die designed for extrusion of AA6063 alloys. These effects may be levelled off after the deoxidising treatment as such or as treatment before the final application of the chromate or cerate conversion coating. For the chemically pretreated AA6005A samples with the same filiform corrosion morphology, i.e. not taking into account the degreasing only series as discussed earlier, the average site density is again the lowest for the chromated samples, showing again the effectiveness of this treatment in view of filiform corrosion initiation characteristics.

Post-extrusion heat treatment
Table 6-6 shows the site density values for the AA6063 series after the additional post-extrusion heat treatments as presented in Table 6-3. The maximum site density for the pot-extrusion heat treated samples is 0.85 for the degreased AA6063-WQ-$\beta'$ condition and a minimum of 0.36 for the AA6063-WQ-WQ-$\beta(3)$ condition.
First, the conditions without the post-extrusion solution heat treatment (AA6063-WQ-WQ and AA6063-WQ-WQ-β(3) conditions) are discussed. The degreased samples show the highest site density values of 0.85 and 0.84 in the AA6063-WQ-β' and the AA6063-WQ-β(3) conditions respectively. The site density increases with site densities of 0.50 and 0.55 for the AA6063-WQ(II) and AA6063-WQ-T6 conditions respectively towards these maximum values and decreases again with coarser precipitate distributions to 0.40 for the AA6063-WQ-β(3) condition, in line with the local attack theory as presented in Chapter 4 of this thesis. The relative response to microstructural variations, characterised by the max/min sdr of 2.13, is relatively large compared to that of 1.31 for the pre-extrusion heat treated samples and will be discussed later.

**Table 6-6:** Site density of post-extrusion heat treated AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-3)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (I)</td>
<td>0.51</td>
<td>0.61</td>
<td>0.51</td>
<td>0.64</td>
</tr>
<tr>
<td>WQ (II)</td>
<td>0.50</td>
<td>0.64</td>
<td>0.51</td>
<td>0.67</td>
</tr>
<tr>
<td>WQ-T6</td>
<td>0.55</td>
<td>0.72</td>
<td>0.55</td>
<td>0.67</td>
</tr>
<tr>
<td>WQ-β'</td>
<td>0.85</td>
<td>0.74</td>
<td>0.58</td>
<td>0.73</td>
</tr>
<tr>
<td>WQ-β(1)</td>
<td>0.84</td>
<td>0.66</td>
<td>0.37</td>
<td>0.70</td>
</tr>
<tr>
<td>WQ-β(2)</td>
<td>0.68</td>
<td>0.62</td>
<td>0.38</td>
<td>0.58</td>
</tr>
<tr>
<td>WQ-β(3)</td>
<td>0.40</td>
<td>0.61</td>
<td>0.38</td>
<td>0.62</td>
</tr>
<tr>
<td>Average sdr</td>
<td>0.64</td>
<td>0.67</td>
<td>0.46</td>
<td>0.66</td>
</tr>
<tr>
<td>Max/min sdr</td>
<td>2.13</td>
<td>1.21</td>
<td>1.57</td>
<td>1.26</td>
</tr>
<tr>
<td>WQ-WQ</td>
<td>0.44</td>
<td>0.62</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>WQ-WQ-β(3)</td>
<td>0.36</td>
<td>0.65</td>
<td>0.67</td>
<td>0.84</td>
</tr>
</tbody>
</table>

A similar trend of decreasing site density with coarsening of the precipitate distribution is
observed for the deoxidised samples with the maximum site density for the deoxidised AA6063-WQ-β' of 0.74. Again the site density increases from 0.64 for the AA6063-WQ(II) condition via 0.72 for the AA6063-WQ-T6 towards the maximum for the AA6063-WQ-β' condition. The max/min sdr of 1.21 indicates a small if any sensitivity for local microstructural changes for the deoxidised samples compared to that for the degreased samples.

The chromated samples show apparent minimum site densities of 0.37-0.38 for the three β conditions, β(1), β(2) and β(3). Microstructural effects are masked in this case by the very effective chromating treatment. The maximum site density of 0.58 is again observed for the AA6063-WQ-β' condition. The site densities on the samples in the AA6063-WQ-T6 and AA6063-WQ(II) conditions are again slightly lower in the order 0.51 and 0.55 respectively. The max/min sdr is 1.57 for the chromated test samples.

Finally, also the cerated AA6063 samples show a maximum site density for the AA6063-WQ-β' condition. The site density decreases for the three β-conditions but not clearly in the order β(1) (0.70) towards β(2) (0.58) and β(3) (0.62). However the general trend is obvious. Again the microstructural effect seems to level off for the cerated samples indicated by a relatively low max/min sdr of 1.26. The degreased test samples show the largest microstructural effect (max/min sdr of 2.13) as this effect is not masked by a surface pretreatment. The chromating treatment also shows a relatively high microstructural effect (max/min sdr of 1.57) compared to the deoxidised (1.21) and cerated samples (1.26). While the degreased, deoxidised and cerated samples show similar levels of average site density (0.64, 0.67 and 0.66 respectively), the chromated samples show a significantly lower average site density of 0.46. Also for the post-extrusion heat treated samples the chromating proves to be the most effective surface pretreatment.

After post-extrusion solution heat treatment, the site density for the degreased test samples is significantly reduced, both in the AA6063-WQ-WQ condition (0.44) and in the AA6063-WQ-WQ-β(3) condition (0.36). This indicates possible influencing of the filiform corrosion initiation characteristics by the thermally grown thick oxide layer after solution heat treatment at 565°C for 6 hours followed by a cold water quench. The deoxidised and chromated samples show similar levels of site density in both conditions varying from 0.62-0.68. The cerated AA6063-WQ-WQ-β(3) sample shows a remarkably high site density of 0.84 compared to the AA6063-WQ-WQ sample (0.63) and the average site density of the other cerated samples (0.66).

Now the site density of the AA6063-WQ(I) condition from the first test series with a pre-
extrusion heat treatment with the site density of the AA6063-WQ(II) condition of the second series with a post-extrusion heat treatment can be compared for the different surface pretreatments. This comparison shows that the difference between the site density values of these two series for the same pretreatments is very small and similar test and analysis conditions for the two series can be assumed. Further analysis of the two series shows that no extreme differences between the average site densities for both series can be observed. The degreased samples after post-extrusion heat treatment show relatively the largest effects of microstructural variations expressed by the high max/min sdr of 2.13. Also the chromated samples for both the pre-extrusion heat treated and post-extrusion heat treated samples show relatively large microstructural effects with max/min sdr of 1.56 and 1.57 respectively. The microstructural effect for the deoxidised samples is largest for the pre-extrusion heat treated samples with a max/min sdr of 1.59 compared to that of 1.21 for the post-extrusion heat treated samples. The microstructural variations are relatively best masked by the cerating treatment.

6.3.4 Average filament length

Pre-extrusion heat treatment

Table 6-7 shows the average filament lengths, indicating the filiform corrosion propagation tendency for the pre-extrusion heat treated samples. A maximum average filament length for the AA6063 samples of 4.29 mm is found in the AA6063-WQ(I) condition. A minimum of 0.85 mm occurred for the chromated AA6063-WQ(I) sample. Large differences between the average filament lengths for the degreased samples and the other three surface pretreatments can be observed. The average filament lengths in the degreased, deoxidised, chromated and cerated state are 4.07, 1.11, 0.92 and 1.21 respectively. The chromating proves to be very effective in reducing the filiform corrosion propagation characteristics for this set of samples. Remarkably the cerated samples showed a slightly higher average filament length than the deoxidised samples.

A very small if any relative microstructural effect is observed for all pretreatments. As for the site density values the cerating shows the smallest if any microstructural effect for the average filament length. A clear microstructural effect trend could not be observed in the results for the four pretreatments.

Also the exposed AA6005A samples do not show a clear microstructural effect trend. The degreased samples again show much higher average filament lengths than the deoxidised,
chromated and cerated samples. The samples in the deoxidised, chromated or cerated state are rather insensitive for the alloy condition. The chromated AA6005A samples show the lowest average filament lengths.

**Table 6-7:** Average filament length [mm] of pre-extrusion heat treated AA6005A and AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-2 and average afl and max/min aflr are defined in the text)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AA6063</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (1)</td>
<td>4.29</td>
<td>1.09</td>
<td>0.85</td>
<td>1.17</td>
</tr>
<tr>
<td>B'</td>
<td>4.03</td>
<td>0.95</td>
<td>0.87</td>
<td>1.19</td>
</tr>
<tr>
<td>B(1)</td>
<td>4.20</td>
<td>1.19</td>
<td>0.91</td>
<td>1.19</td>
</tr>
<tr>
<td>B(2)</td>
<td>4.06</td>
<td>1.23</td>
<td>1.00</td>
<td>1.26</td>
</tr>
<tr>
<td>B(3)</td>
<td>3.78</td>
<td>1.07</td>
<td>0.98</td>
<td>1.25</td>
</tr>
<tr>
<td>Average afl</td>
<td>4.07</td>
<td>1.11</td>
<td>0.92</td>
<td>1.21</td>
</tr>
<tr>
<td>Max/min aflr</td>
<td>1.13</td>
<td>1.29</td>
<td>1.18</td>
<td>1.08</td>
</tr>
<tr>
<td><strong>AA6005A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B'</td>
<td>4.58</td>
<td>1.26</td>
<td>1.02</td>
<td>1.33</td>
</tr>
<tr>
<td>B(1)</td>
<td>3.56</td>
<td>1.31</td>
<td>1.09</td>
<td>1.30</td>
</tr>
</tbody>
</table>

**Post-extrusion heat treatment**

Also after post-extrusion heat treatment large differences in the average filament lengths for the different tested samples can be found, as presented in Table 6-8. The degreased samples show by far the highest average filament lengths compared to the other three pretreatments. A maximum average filament length of 5.14 mm was found for the degreased AA6063-WQ-B' sample and a minimum of 0.93 mm for the chromated AA6063-WQ(II) sample.

Analysis of the average propagation properties for each pretreatment shows that chromating again proves to be the most effective with an average of 1.08 mm, compared to similar levels of average propagation for the deoxidised (1.53 mm) and cerated (1.49 mm)
samples and the high average propagation of 4.03 mm for the degreased samples.

**Table 6-8:** Average filament length of post-extrusion heat treated AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-3)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (I)</td>
<td>4.29</td>
<td>1.09</td>
<td>0.85</td>
<td>1.17</td>
</tr>
<tr>
<td>WQ (II)</td>
<td>4.21</td>
<td>1.12</td>
<td>0.93</td>
<td>1.14</td>
</tr>
<tr>
<td>WQ-T6</td>
<td>4.23</td>
<td>1.40</td>
<td>1.11</td>
<td>1.33</td>
</tr>
<tr>
<td>WQ-β'</td>
<td>5.14</td>
<td>1.95</td>
<td>1.46</td>
<td>1.64</td>
</tr>
<tr>
<td>WQ-β(1)</td>
<td>4.56</td>
<td>1.79</td>
<td>1.05</td>
<td>1.66</td>
</tr>
<tr>
<td>WQ-β(2)</td>
<td>2.86</td>
<td>1.50</td>
<td>0.96</td>
<td>1.68</td>
</tr>
<tr>
<td>WQ-β(3)</td>
<td>3.17</td>
<td>1.44</td>
<td>0.99</td>
<td>1.47</td>
</tr>
<tr>
<td>Average afl</td>
<td>4.03</td>
<td>1.53</td>
<td>1.08</td>
<td>1.49</td>
</tr>
<tr>
<td>Max/min aflr</td>
<td>1.80</td>
<td>1.74</td>
<td>1.57</td>
<td>1.47</td>
</tr>
</tbody>
</table>

For all surface pretreatments a very clear microstructural effect can be observed. The maximum average filament length is observed for the AA6063-WQ-β' sample and decreases with coarsening of the precipitate distribution fully in line with the theory presented in Chapter 4. From the pre-extrusion solutionised as extruded condition (AA6063-WQ(II)) via the AA6063-WQ-T6 condition the average filament length increases towards this maximum for the AA6063-WQ-β' sample. The quantitative trends for each surface pretreatment are clearly shown in Table 6-8. This trend is also expressed in the max/min aflr for the degreased, deoxidised, chromated and cerated samples. These ratios are far higher than those for the pre-extrusion heat treated test series: the extrudates are more sensitive to post-extrusion heat treatments than for the same heat treatments before extrusion. This is in line with the microstructural observations presented in section 6.3.1
and as analysed in [6.1] showing little differences in microstructure for the AA6063 series after extrusion when a pre-extrusion heat treatment was applied. This is related to (partial) dissolution of the created Mg$_2$Si precipitate phases during hot extrusion. When such a Mg$_2$Si phase distribution is created after extrusion it is still present when corrosion testing takes place and results are far more sensitive to these microstructural variations.

For the degreased samples, after the post-extrusion solution heat treatment the average filament lengths are smaller than for the other samples. Possibly, the thick thermally grown oxide layer on these surfaces, besides microstructural effects, may have contributed to this decrease in average filament lengths. After chromating the average filaments are the smallest.

### 6.3.5 Corrosion number

**Pre-extrusion heat treatment**

The total attack, defined as the corrosion number, for all pre-extrusion heat treated samples is presented in Table 6-9.

As the trends for the site density and average filament length with thermal treatments and surface treatments are comparable, the quantification using the corrosion number yields little additional insight.

For the degreased samples the corrosion number slowly decreases from the maximum of 2.82 for the AA6063-β(1) condition to lower values of 2.21 and 2.07 for the AA6063-β(2) and AA6063-β(3) conditions respectively.

For the deoxidised samples also a trend of decreasing corrosion number with a coarser pre-extrusion precipitate distribution can be observed.

The chromated samples show low absolute values of the corrosion number but no clear trend in a decreasing corrosion number with a coarser pre-extrusion precipitate distribution.

For the cerated test series little differences between the various microstructures are observed, resulting in a lower max/min cnr.

By far the highest average corrosion number of 2.38 is observed for the degreased samples, compared to the lower average corrosion numbers of 0.66, 0.48 and 0.77 for the deoxidised, chromated and cerated samples. Chromating proves to be the most effective surface pretreatment for this test series.
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6xxx

Table 6-9: Corrosion number of pre-extrusion heat treated AA6005A and AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-2 and average cn and max/min cnr are defined in the text)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AA6063</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (1)</td>
<td>2.18</td>
<td>0.66</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>β'</td>
<td>2.64</td>
<td>0.74</td>
<td>0.55</td>
<td>0.76</td>
</tr>
<tr>
<td>β(1)</td>
<td>2.82</td>
<td>0.73</td>
<td>0.50</td>
<td>0.76</td>
</tr>
<tr>
<td>β(2)</td>
<td>2.21</td>
<td>0.60</td>
<td>0.54</td>
<td>0.84</td>
</tr>
<tr>
<td>β(3)</td>
<td>2.07</td>
<td>0.57</td>
<td>0.40</td>
<td>0.75</td>
</tr>
<tr>
<td><strong>Average cn</strong></td>
<td>2.38</td>
<td>0.66</td>
<td>0.48</td>
<td>0.77</td>
</tr>
<tr>
<td><strong>Max/min cnr</strong></td>
<td>1.36</td>
<td>1.30</td>
<td>1.38</td>
<td>1.14</td>
</tr>
<tr>
<td><strong>AA6005A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β'</td>
<td>1.25</td>
<td>0.84</td>
<td>0.66</td>
<td>1.03</td>
</tr>
<tr>
<td>β(1)</td>
<td>1.56</td>
<td>0.93</td>
<td>0.57</td>
<td>0.94</td>
</tr>
</tbody>
</table>

The pre-extrusion heat treated samples show relatively low sensitivity to microstructural variations compared to the post-extrusion heat treated samples as discussed later in this subparagraph. The max/min cnr for the degreased, deoxidised, chromated and cerated samples are 1.36, 1.30, 1.38 and 1.14. Especially the cerated samples show the most levelling off of the corrosion number.

Post-extrusion heat treatment

The corrosion numbers, indicating the total filiform corrosion attack, for the post-extrusion heat treated samples are presented in Table 6-10. Also for these test series the degreased samples show the highest corrosion numbers compared to those for the other three pretreatments. A maximum corrosion number of 4.37 is found for the degreased AA6063-WQ-β' condition and a minimum of 0.37 for the chromated AA6063-WQ-β(2) and AA6063-WQ-β(3) samples.

Analysis of the average corrosion number for each surface pretreatment shows that
chromating again proves to be the most effective. The average corrosion numbers after a post-extrusion heat treatment are higher than those after a pre-extrusion heat treatment for all surface pretreatments.

For all surface pretreatments a very clear microstructural effect already reported both for the site densities and average filament lengths, can be observed. The quantitative trends for each surface pretreatment are clearly shown in Table 6-10. These max/min cnr ratios are far higher than those for the pre-extrusion heat treated test series: the extrudates are more sensitive to post-extrusion heat treatments than for the same heat treatments before extrusion. The relative microstructural effect is the largest for the least masking pretreatment, the degreasing pretreatment. The cerating treatment levels off the microstructural effect the most.

Table 6-10: Corrosion number of post-extrusion heat treated AA6063 with variation of heat treatment and surface pretreatment (the alloy condition codes are listed in Table 6-3)

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>degreased</th>
<th>deoxidised</th>
<th>chromated</th>
<th>cerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WQ (I)</td>
<td>2.18</td>
<td>0.66</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>WQ (II)</td>
<td>2.11</td>
<td>0.72</td>
<td>0.47</td>
<td>0.77</td>
</tr>
<tr>
<td>WQ-T6</td>
<td>2.33</td>
<td>1.01</td>
<td>0.61</td>
<td>0.89</td>
</tr>
<tr>
<td>WQ-β'</td>
<td>4.37</td>
<td>1.45</td>
<td>0.84</td>
<td>1.19</td>
</tr>
<tr>
<td>WQ-β(1)</td>
<td>3.84</td>
<td>1.19</td>
<td>0.39</td>
<td>1.16</td>
</tr>
<tr>
<td>WQ-β(2)</td>
<td>1.94</td>
<td>0.93</td>
<td>0.37</td>
<td>0.98</td>
</tr>
<tr>
<td>WQ-β(3)</td>
<td>1.28</td>
<td>0.87</td>
<td>0.37</td>
<td>0.91</td>
</tr>
<tr>
<td>Average cn</td>
<td>2.65</td>
<td>1.03</td>
<td>0.51</td>
<td>0.98</td>
</tr>
<tr>
<td>Max/min cnr</td>
<td>3.41</td>
<td>2.01</td>
<td>2.27</td>
<td>1.55</td>
</tr>
<tr>
<td>WQ-WQ</td>
<td>1.27</td>
<td>0.86</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>WQ-WQ-β(3)</td>
<td>1.16</td>
<td>1.05</td>
<td>0.89</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Finally, after post-extrusion solution heat treatment the corrosion number for the degreased samples is low compared to the other samples: the AA6063-WQ-WQ and AA6063-WQ-
The effect of pre- and post-extrusion heat treatment on the filiform corrosion properties of AA6xxx

WQ-β(3) samples show corrosion numbers of 1.27 and 1.16. Besides the microstructural effect also the thermally grown thick oxide layer on these degreased only samples may play a role in the low corrosion numbers.

Comparing the corrosion numbers of the AA6063-WQ(I) condition from the first test series with a pre-extrusion heat treatment with the corrosion numbers of the AA6063-WQ(II) condition of the second series with a post-extrusion heat treatment indicates that similar test and analysis conditions for the two series can be assumed.

6.3.6 Potentiodynamic polarisation measurements

For the post-extrusion heat treated AA6063 alloys the characteristic potentiodynamic polarisation scans in both the anolyte and the catholyte are shown in Figure 6-5(a) to 6-5(f). The characteristic potentials and the filiform corrosion currents derived from the potentiodynamic polarisation measurements are listed in Table 6-11. The correlation of the filiform corrosion current derived from the potentiodynamic polarisation measurements and the filiform corrosion tests is discussed in section 6.3.7.

The OCPs of the samples in the various heat treatment conditions show little difference in the anolyte. The lowest value of –0.87 V vs SCE is derived for the AE-condition and the highest value of –0.79 V vs SCE for the β'-condition: a maximum difference of 0.08 V. The pitting potentials for the different conditions all lie in the range of –0.75 V vs SCE to –0.79 V vs SCE: a maximum difference of 0.04 V. The most homogeneous alloy condition, the AE-condition, showed the largest passive range of 0.12 V under anolyte conditions. For the β'-condition, the OCP and pitting potential co-incide (passive range 0.00 V).

The OCPs in the catholyte show a larger variation than those in the anolyte for the set of samples tested. The lowest value of –0.69 V vs SCE β(3)-condition is –0.36 V lower than the highest value of –0.33 V vs SCE in the β(1)-condition. Another important observation is the initial increase of the cathodic current in the catholyte from the AE-condition to the β'- and β(1)-condition and the decrease of cathodic current and OCP from the β(1)-condition to the β(3)-condition. Furthermore, Figures 6-5(a) to 6-5(f) show that if the cathode surface area is taken equal to the anode area (i.e. the catholyte curve shifts two orders of magnitude to the left because of the current surface area ratio of 100), the electrical current in the catholyte is always much lower than that in the anolyte at the same potential. This mainly originates from the availability of hydrogen ions in the anolyte.
Figure 6-5: (a) to (f) show the typical potentiodynamic polarisation measurements for the AE, T6, β', β(1), β(2) and β(3) conditions respectively.
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The filiform corrosion current shows values increasing from the AE-condition \((2.2 \times 10^{-5} \text{ A})\) to maximum values for the the \(\beta^-\) and \(\beta(1)\)-condition \((1.3 \times 10^{-4} \text{ A})\) and decreasing from these values towards the \(\beta(3)\)-condition \((2.3 \times 10^{-5} \text{ A})\).

**Table 6-11:** Summary of the characteristic potential and filiform corrosion current values for the post-extrusion heat treated AA6063 alloys under anolyte and catholyte conditions.

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Open Circuit Potential vs. SCE [V]</th>
<th>Pitting Potential vs. SCE [V]</th>
<th>Passive range [V]</th>
<th>Filiform Corrosion Current [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE</td>
<td>-0.87</td>
<td>-0.59</td>
<td>0.12</td>
<td>2.2 \times 10^{-5}</td>
</tr>
<tr>
<td>T6</td>
<td>-0.81</td>
<td>-0.45</td>
<td>0.05</td>
<td>6.7 \times 10^{-5}</td>
</tr>
<tr>
<td>(\beta^-)</td>
<td>-0.79</td>
<td>-0.56</td>
<td>0.00</td>
<td>1.3 \times 10^{-4}</td>
</tr>
<tr>
<td>(\beta(1))</td>
<td>-0.82</td>
<td>-0.33</td>
<td>0.06</td>
<td>1.3 \times 10^{-4}</td>
</tr>
<tr>
<td>(\beta(2))</td>
<td>-0.82</td>
<td>-0.45</td>
<td>0.05</td>
<td>5.9 \times 10^{-5}</td>
</tr>
<tr>
<td>(\beta(3))</td>
<td>-0.81</td>
<td>-0.69</td>
<td>0.06</td>
<td>2.3 \times 10^{-5}</td>
</tr>
</tbody>
</table>

### 6.3.7 Combination of potentiodynamic polarisation and filiform corrosion results

As for the combined potentiodynamic polarisation and filiform corrosion study presented in Chapter 3, one has to keep in mind that the filiform corrosion current in real filaments could differ significantly from the presented values, depending on the actual anodic and cathodic areas and the effective cathode/anode area ratio in real filaments. However, assuming a similar effective cathode/anode area ratio for the alloys investigated, the correlation between the filiform corrosion current and the filiform corrosion properties would still apply. Also it has to be noted that in the present analysis the filiform corrosion current is related to one-dimensional propagation rates of the filaments when filament width and in-depth attack are considered to be constant for comparable systems. Furthermore, the present analysis does not take into account the electrolyte resistance between the anodic and cathodic sites in real filaments.

The correlation between the filiform corrosion characteristics and filiform corrosion current is presented in Figure 6-6 for the degreased post-extrusion heat treated AA6063
alloys. The filiform corrosion currents and relevant potentials are also summarised in Table 6-11.

![Graph](image)

**Figure 6-6:** The correlation between the filiform corrosion current and the average filament length (a) and the corrosion number (b) for the degreased post-extrusion heat treated AA6063 alloys.

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Figure 6-6(a) shows the following trend for the tested AA6063 alloys: a higher filiform corrosion current corresponds with a higher average filament length after 1000 hours of accelerated exposure.

The increase in the filiform corrosion current with filiform corrosion susceptibility mainly results from the changes in the cathodic curves in the catholyte, i.e. OCP and cathodic current, while the anodic and cathodic curves in the anolyte do not show large differences, besides the relatively high passive range for the AE-condition (0.12 V) and the absence of a passive range for the $\beta^*$-condition.

![Graph showing site density as a function of passive range](image)

**Figure 6-7:** The site density for the degreased post-extrusion heat treated AA6063 alloys as a function of the passive range in the anolyte.

The variation in the passive range of the alloys tested under anolyte conditions as mentioned just above adds to the correlation between the potentiodynamic polarisation measurements and the filiform corrosion susceptibility, as can be further derived from Figure 6-7. In Chapter 3 it was discussed that a smaller passive range corresponds to more rapid pitting and hence to a higher number of filiform corrosion initiations per scratch length, in this chapter defined as the site density parameter. For the $\beta^*$-condition the pitting potential co-incides with the OCP, whereas the AE-condition showed a more distinct difference between the pitting potential and the OCP (0.12 V). If the ease of filiform
corrosion initiation is related to the ease of pitting for a specific alloy, this would explain the higher site density for the β'-condition (0.86) compared to that for the AE-condition (0.50). The site density as a function of the passive range for all conditions is presented in Figure 6-7. This figure shows that the correlation between the passive range and the site density is most clear for the β'-condition, which is the most sensitive condition to filiform corrosion initiation, and the less sensitive AE-condition, and however the others do not particularly show such a distinct correlation, they also do not contradict such a correlation. The observed relative filiform corrosion behaviour on the alloys tested can be rationalised by a more detailed analysis of the information in the potentiodynamic diagram shown schematically in Figure 6-8 for a hypothetical set of alloys.

**Figure 6-8:**  *Schematic representation of the potentiodynamic polarisation curves in the anolyte and catholyte solutions*

Curve ‘A’ indicates an increasing cathodic reduction reaction rate in the catholyte, resulting in an increasing filiform corrosion current. Curve ‘B’ indicates a decreasing passive range under anolyte conditions which we have related to the filiform corrosion initiation characteristics in Figure 6-7: a smaller passive range corresponds to more rapid pitting and hence to a higher number of filiform corrosion initiations per scratch length. Figure 6-8 also shows that a decreasing passive range results in an increasing filiform corrosion current under similar catholyte conditions. The increased ease of pitting will also enhance
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the propagation rate. The supposed correlation between the ease of pitting and the ease of filiform corrosion initiation and propagation is best expressed by the very clear trend of the increasing filiform corrosion current with the corrosion number as shown in Figure 6-6(b). This Figure 6-6(b) combines the effects of the observed trends of vectors ‘A’ and ‘B’ on both the initiation and propagation behaviour for the alloys tested.

Detailed analysis of the potentiodynamic polarisation curves for the binary Al-Cu alloy in Figure 3-1(a) shows that the trends of the cathodic curves in the catholyte and the passive range in the anolyte correspond to the trends of vectors A and B shown in Figure 6-8. For the Al-1.00Cu alloy the cathodic current in the catholyte was higher and the passive range in the anolyte smaller compared to those for the Al-0.20Cu alloy. Also for these Al-Cu alloys these trends correspond to an increasing filiform corrosion propagation and initiation sensitivity, as shown in Figures 3-3, 3-4 and 3-6, which is similar to the results for the technical post-extrusion heat treated AA6063 alloys presented in this section.

6.4 Discussion

In the previous paragraph the microstructural analysis of the billets and extrudates, the filiform corrosion morphology and the quantitative filiform corrosion analysis is presented. The microstructural analysis and the parallel DSC-experiments [6.1] all indicate that both for the billets and extrudates, the Mg₂Si phase and precipitate distribution can be influenced with variation of pre- and post-extrusion heat treatments. The solution heat treatment at 565°C for 6 hours followed by a cold water quench results in a maximum concentration of alloying elements in solid solution. A subsequent heat treatment at 250°C for 24 hours results in the formation of β’ semi-coherent phases and for the heat treatments at 325°C, 400°C and 450°C for 24 hours the formations of incoherent β-phases takes place, with coarsening of the β-distribution with increasing temperature. When these heat treatments are applied on the billets before extrusion, the created microstructural variations (partially) level off to more or less equal post-extrusion alloy conditions, due to the (partial) dissolution of Mg₂Si phases during the hot extrusion process, and differences disappear. The lower average filiform corrosion initiation and propagation susceptibility and a smaller relative microstructural effect for the pre-extrusion heat treated samples compared to those for the post-extrusion heat treated samples can be attributed to the (partial) dissolution of the created Mg₂Si phases during hot extrusion.
Chapter 6

A correlation between the polarisation measurements and both filiform corrosion propagation and total attack after the accelerated exposure test for the post-extrusion heat treated samples is observed. The observed correlations for the alloys tested can be explained from the electrochemical response to local variations of the substrate composition. This chapter and the previous chapters have shown that the type of alloying elements, their concentration and distribution largely influence the filiform corrosion properties of the alloy. The observed correlation is fully in line with this theory and with coarsening of the Mg2Si precipitate distribution the filiform corrosion susceptibility of the tested alloys decreases. The effect of the concentration of cathodic or anodic particles and their distribution was presented schematically in Figure 4-10. For a fine distribution of particles (in this case Mg2Si) it is likely that other 'fresh' cathodic particles are more rapidly reached by the corroded zone around these particles, which in turn will participate in the substrate matrix dissolution. A large cathodic surface area will participate in the matrix dissolution process for a fine distribution of cathodic particles, related to the, small in an absolute sense but significant, in-depth attack during the corrosion process. The increased cathodic area will therefore lead to an increasing cathodic current, a rapid spread of the corrosion front and thus a high filiform corrosion propagation rate. Such an increasing filiform corrosion susceptibility is perfectly expressed by an increasing filiform corrosion current in the present study. This magnitude of the filiform corrosion current for the present set of alloys is determined by a combination of observed trends for the cathodic current in the catholyte and the passive range in the anolyte with variation of the particle distribution. The potentiodynamic polarisation measurements under catholyte conditions show an initial increase of the cathodic current from the AE-condition to the β'- and β(1)-condition and a decrease of cathodic current and OCP from the β(1)-condition to the β(3)-condition. The most homogeneous alloy condition, the AE-condition, showed the largest passive range under anolyte conditions. For the β'-condition, the OCP and pitting potential co-incide. The highest filiform corrosion current is derived for the β'-conditions and this tendency decreases with coarsening of the precipitate distribution from the β(1)- to the β(3)-conditions. For the alloys tested the filiform corrosion initiation characteristics are related to the passive range and thus implicitly to the ease of pitting of the alloy. A smaller passive range tends to correlate with a higher filiform site density for the alloys tested. The supposed correlation between the ease of pitting and the ease of filiform corrosion initiation and propagation is best expressed by the very clear trend of the increasing filiform corrosion
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current with the corrosion number.
Detailed analysis of the potentiodynamic polarisation curves for the binary Al-Cu alloy in Chapter 3 shows that the trends of the cathodic curves in the catholyte and the passive range in the anolyte correspond to the trends observed for the post-extrusion heat treated AA6063 alloys. A higher cathodic current in the catholyte and a smaller passive range with increasing copper concentration was observed for the Al-Cu alloys. Also for these Al-Cu alloys these trends correspond to an increasing filiform corrosion propagation and initiation sensitivity which is similar to the results for the post-extrusion heat treated AA6063 alloys showing increasing sensitivities with a finer particle distribution. A filiform corrosion hampering mechanism similar to that observed for the binary Al-Zn alloys because of the decreasing cathodic current (hydrogen reduction reaction) under anolyte conditions with increasing zinc concentration is not observed for the post-extrusion heat treated AA6063 samples.

The degreased samples show the highest average filament lengths compared to the deoxidised, chromated and cerated samples. Besides longer filaments, the degreased samples show wider and more shallow attack compared to those for the other surface pretreatments. On the deoxidised, chromated and cerated surfaces the filaments show a more rugged and pronounced filiform corrosion morphology with a recurrent necking or closely packed blister propagation pattern along the filament tail. This pattern is less clear for the only degreased samples due to the smoother filiform corrosion attack morphology. The observation of recurrent necking supports an apparent stepwise filiform propagation. The differences in filament height and width between the degreased samples on the one hand and the deoxidised, chromated and cerated ones on the other hand are due to differences in the adhesion strength between the organic coating and the substrate surface. For a relatively low adhesion strength (degreased samples) the filament volume increase by the build-up of corrosion product is accommodated by delamination of the organic coating at the edges of the filament preferred to stretching of the organic coating. This results in relatively flat and wide filaments. For higher adhesion strengths (deoxidised, chromated and cerated samples), the filament volume increase is accommodated by coating stretching preferred to coating delamination, resulting in relatively narrow and high filaments.

Deoxidising the surface influences the filiform corrosion propagation to a large extent for all tested alloy conditions. The top surface layer of the tested alloys prove to be very susceptible to filiform corrosion. After removal of this surface layer by deoxidising, the susceptibility can be further reduced by the presence of a chromate pretreatment layer. The
active chromate layer reduces both the initiation and propagation of filaments. However cerating does not further improve the filiform corrosion susceptibility after deoxidising in an absolute sense, the relative microstructural effects are levelled off.

6.5 Conclusions

Heat treatment of AlMgSi alloys can influence the filiform corrosion properties significantly. When a heat treatment is applied before extrusion the relative microstructural effect on the filiform corrosion properties is smallest, due to (partial) dissolution of the precipitate distributions created during hot extrusion. The alloys are most susceptible to filiform corrosion in the B'-condition and this susceptibility decreases with coarsening of the Mg2Si particle distribution.

Degreasing only of the alloy surfaces gives the longest and widest filaments, as well as the most shallow filiform corrosion morphology, compared to the deoxidised, chromated and cerated samples, related to a lower adhesion strength of the organic coating for the degreased samples compared to that for the otherwise pretreated samples. Deoxidising the surface reduces the filiform corrosion propagation to a large extent for all tested alloy conditions, indicating a susceptible top surface layer. The filiform corrosion susceptibility can be further reduced by chromating after removal of the susceptible surface layer with the deoxidising treatment. The active chromate layer reduces both the initiation and propagation of filaments. From the present results it can be concluded that cerating does not further improve the filiform corrosion susceptibility after deoxidising in an absolute sense, but the relative microstructural effects are levelled off.

A correlation between the polarisation measurements and both filiform corrosion propagation and total attack after the accelerated exposure test for the post-extrusion heat treated AA6063 samples is observed. The observed correlations for the alloys tested can be explained from the electrochemical response to the variations of the Mg2Si particle distribution. For equivalent particle volumes, a large cathodic surface area will participate in the matrix dissolution process for a fine distribution of cathodic particles, related to the, small in an absolute sense but significant, in-depth attack during the corrosion process. The increased cathodic area will therefore lead to an increasing cathodic current, a rapid spread of the corrosion front and thus a high filiform corrosion propagation rate. Such an increasing filiform corrosion susceptibility is perfectly expressed by an increasing filiform
corrosion current in the present study. The magnitude of the filiform corrosion current for
the present set of alloys is determined by a combination of observed trends for the cathodic
current in the catholyte and passive range under anolyte conditions with variation of the
particle distribution. The highest filiform corrosion current is derived for the $\beta'$-conditions
and this tendency decreases with coarsening of the precipitate distribution from the $\beta(1)$- to
the $\beta(3)$-conditions.

For the alloys tested the filiform corrosion initiation characteristics are related to the
passive range and thus implicitly to the ease of pitting of the alloy. A smaller passive range
tends to correlate with a higher filiform site density for the alloys tested. The supposed
correlation between the ease of pitting and the ease of filiform corrosion initiation and
propagation is best expressed by the very clear trend of the increasing filiform corrosion
current with the corrosion number.

References

6.5 H. LETH-OLSEN and K. NISANCIIOGLU, Corrosion 53 (1997) p. 705
6.11 Deutsches Institut Für Normung e.V., Number 65472: Filiform corrosion test of
coatings on aluminium alloys, draft (1989)
Chapter 6


6.13 H. LETH-OLSEN, PhD-Thesis, Department of Electrochemistry of the Norwegian University of Science and Technology (1996)

Summary

This thesis describes the results of a number of combined filiform corrosion and potentiodynamic polarisation measurements on a range of binary alloys and industrial alloys with the aim of elucidating the effects of microstructural variations in the substrate. In Chapter 1 current knowledge concerning filiform corrosion including effects of the substrate, surface pretreatment and organic coating, as reported in the literature are summarised and structured. Special attention is paid to the electrochemical reactions taking place at the coating-substrate interface.

The accelerated filiform corrosion exposure tests on eleven binary and one ternary model alloy described in Chapter 2 show and quantify the compositional and pretreatment effects on the filiform corrosion behaviour of the tested substrates. For all binary alloys, the site density of the filaments increases with increasing concentration of the alloying element in case of a simple degreasing treatment prior to coating application. This trend of an increasing average filament length with the alloying concentration is especially clear for the highly susceptible Al-Cu binary alloys and to a lesser degree for the Al-Si alloys. This is in contrast with the Al-Zn and Al-Mg alloys which show no or little significant increase in average filament length with solute content. Evaluation of the total filiform corrosion attack, defined as the product of the site density and the average filament length, shows that the average corrosion number decreases in the order Al-Cu, Al-Si, Al-Zn, Al-Mg. Furthermore, the corrosion number increases for all binary alloys with the alloying concentration. These observations support the applicability of the fundamental cause of local corrosion processes to filiform corrosion on aluminium alloys. Successive interactions between the alloy matrix and particles are likely to be affected by the alloying elements and their concentrations. The trend of an increasing corrosion number with alloying concentration is particularly clear for the degreased samples. On the chromated and cerated samples the filiform corrosion attack was too small to confirm such a relation with any statistical significance, but the data would not contradict such a conclusion.

While the detailed examination of the filiform corrosion rate as a function of the substrate composition and the surface pretreatment applied, presented in Chapter 2, yields valuable results, it does not provide explanations for observed dependencies. The underlying mechanisms for filiform corrosion can only be elucidated by performing electrochemical

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measurements in media characteristic for the corrosion process studied. To this aim the results of potentiodynamic polarisation measurements in synthetic anolyte and catholyte media, which are characteristic for the local anodic and cathodic sites in the filaments on the aluminium substrates, are discussed in Chapter 3. The potentiodynamic polarisation measurements are performed on two Al-Cu binary alloys and four Al-Zn binary alloys. A correlation between the filiform corrosion current, defined as the intercept of the cathodic curve in the catholyte and the anodic curve in the anolyte, and the average filament length after the accelerated exposure test is observed for the Al-Cu binary alloys. Such a correlation is not observed for the Al-Zn alloys as an increasing filiform corrosion current is barely reflected in a higher average filament length. When comparing the results for the Al-Cu and Al-Zn binary alloys it can be concluded that the correlation differs significantly with the solute atom and the filiform corrosion current as defined turns out to be a non-uniquely discriminating parameter for the filiform corrosion susceptibility of the set of model alloys investigated in the present research. The different correlation factors for the Al-Cu and Al-Zn alloys are explained from the electrochemical response to local variations of the substrate composition. The strong dependency of the filiform corrosion current with the average filament length for the Al-Cu binary alloys is related to the significant increase of the cathodic and anodic reaction rate with increasing Cu concentration. The binary Al-Zn alloys show more constant overall anodic and cathodic reaction rates as a function of the Zn concentration. This is due to a trend of a decreasing cathodic reaction rate in the anolyte, i.e. a reduced hydrogen reduction rate, with increasing Zn concentration, hampering an increase of the filiform corrosion propagation rate. This would explain the increasing average filament length with Cu concentration and the more constant average filament length with increasing Zn concentration after 1000 hours of accelerated exposure testing.

For the Al-Cu and Al-Zn model alloys the filament site density was found to correlate with the magnitude of the passive range and thus implicitly, filiform corrosion initiation seems to be related to the ease of pitting of the alloy. A smaller passive range results in higher filiform site density for both the Al-Cu and Al-Zn alloys.

In Chapter 4 a mechanistic study of filiform corrosion on AA2024-T351 is discussed, with the aim of revealing the general and local mechanism of filiform corrosion on aluminium alloys. The overall mechanism was revealed by Scanning Kelvin Probe measurements which showed corrosion potential variations along filaments from which the anodic undermining mechanism for filiform corrosion on aluminium alloys could be deduced. The
composition of the electrolyte conditions in the very tip of the filament was determined and a synthetic anolyte was designed. This anolyte and corresponding catholyte were used in all potentiodynamic polarisation measurements. The anolyte is characterised by low pH (pH values of 1-2 were measured) and a high chloride concentration. The local high chloride concentration in the very tip of real filaments was confirmed by EDX analysis on scalped samples. In-situ time lapse video observations showed the hydrogen evolution in the filament tip and a stepwise propagation mode of the filament tip. This stepwise growth effect is related to the discontinuous nature of storage of recoverable elastic energy in the organic coating and its release when exceeding the bonding strength. When comparing the filiform corrosion propagation properties of coated systems for similar and well adhering organic coatings and reproducible chemical pretreatments, the differences in average filiform corrosion propagation rates can be attributed to differences in the microstructure of the substrates under investigation, leading to different average anodic undermining rates, with the mechanical stepwise debonding mechanism as a second order effect.

In Chapter 5 the possibility of stimulation of filiform corrosion on exposed surfaces by the presence of (noble) macro defects is investigated and confirmed in filiform corrosion tests on model substrates with either copper-rich line defects or inserted copper pens in drilled holes. From the filiform corrosion tests on the AA2024-T351 with the (copper pen) macro defects it can be concluded that the filiform corrosion initiation and propagation directly adjacent to the (noble) macro defect is stimulated. More and longer filaments are observed at the position of the copper pen macro defects. For the degreased sample, stimulation of the filiform corrosion initiation in the adjacent scratch could not be confirmed, but the deoxidised sample shows a significant increase of the number of filaments in the adjacent scratch. The filiform corrosion propagation in the adjacent scratch is stimulated by the presence of the nearby copper pen, which is in line with observations for model samples with copper-rich line defects. It is clear that the influencing distance of the macro defect, either as a copper-rich line defect or as a copper pen, will not be infinite but is estimated to be limited to the order of about one to a few centimeters for the present sample and defect configurations. The observations show that relatively long distance effects due to the presence of noble artificial macro defects can promote filiform corrosion in a manner effectively similar to that of noble local intermetallics.

These observations implicitly confirm the local substrate attack model presented in this thesis. It shows the importance of the presence of cathodically active phases (such as the copper-rich (macro) phases for the model substrates tested) in particular at the substrate
surface for the filiform corrosion attack, fully in line with the observations reported for the binary model alloys. In the absence of such cathodic phases, the cathodic reaction is not stimulated and substrates prove to be much less susceptible to filiform corrosion. For degreased model substrates with magnesium-rich line defects, filiform corrosion did not initiate at the position of the magnesium-rich line defects independent of the subsurface magnesium concentration. In the case of the presence of anodic phases, such as the magnesium-rich macro phases, rapid matrix dissolution is not likely. The anodic phases will dissolve preferentially leaving behind a relatively homogeneous substrate surface. In the absence of noble heterogeneities in the substrate surface, localised corrosion by the formation of microgalvanic couples will not occur, leading to a relatively low substrate surface attack rate, also not very much depending on the concentration of the anodic particles.

Investigation on surface treated AA2024-T351 samples shows that the filiform corrosion propagation direction for as rolled surfaces is preferentially in the rolling direction. For mechanically surface treated substrates the preferential filiform corrosion propagation direction is in the direction of the mechanical grinding and polishing. Two new qualitative chemistry and geometry based mechanisms are proposed in this chapter to explain the preferential propagation direction. The chemical effect of rolling, grinding and working is attributed to the alignment of particles (i.e. precipitates, dispersoids and constituent particles) in this direction and thus a higher concentration and/or finer distribution of particles will be present in this direction. The increased cathodic area will therefore lead to rapid spread of the corrosion front in this direction and thus a high filiform corrosion propagation rate relative to the other directions. In addition, from classical crack tip propagation theory, assuming equal chemical substrate surface conditions and mechanical pressure in the filament tip in all directions, it can be concluded that the ‘crack tip’, in this case the filament tip, is likely to open and propagate in the direction of the sharp notch (small angle of incidence) and thus in the direction of rolling, grinding or working. The relative contributions of the chemical and geometrical effects are still subject of further investigation and discussion.

Application of specific surface patterns on AA2024-T351 substrates is shown to be a very effective way of confining and restricting filiform corrosion attack within the set boundaries by the surface pattern.

Finally in Chapter 6 the results of a study on the effects of pre- and post-extrusion heat treatments on the filiform corrosion susceptibility of two widely used commercial
aluminium alloys AA6063 and AA6005 are described. The thermal treatments and the
extrusions were performed under industrial conditions. The organic coatings were applied
in a laboratory environment. The results indicate that coarsening of the Mg$_2$Si precipitate
distribution leads to a decrease in the filiform corrosion susceptibility of the tested alloys.
The highest filiform corrosion susceptibility is determined for the $\beta^+$-conditions and this
susceptibility decreases with coarsening of the precipitate distribution from the $\beta(1)$- to the
$\beta(3)$-conditions irrespective of the chemical pretreatment. This microstructural effect on
the site density, the average filament length and the resulting corrosion number is the
largest for the post-extrusion heat treated samples. When comparing the results for the
various pre-extrusion heat treatments much smaller but still significant effects were
observed. The relatively small magnitude of the effect can be explained by the (partial)
dissolution of the different precipitate distributions during hot extrusion leading to a more
or less comparable metallurgical state for the as-extruded material.
For the set of post-extrusion heat treated set of samples, a correlation between the
potentiodynamic polarisation measurements and both filiform corrosion propagation and
total attack after the accelerated exposure test is observed. The observed correlations for
the alloys tested can be explained from the electrochemical response to local variations of
the substrate composition. For equivalent particle volumes, a large cathodic surface area
will participate in the matrix dissolution process for a fine distribution of cathodic
particles, related to the, small in an absolute sense but significant, in-depth attack during
the corrosion process. An increased cathodic area will therefore lead to an increasing
cathodic current, a rapid spread of the corrosion front and thus a high filiform corrosion
propagation rate. Such an increasing filiform corrosion susceptibility is well expressed by
an increasing filiform corrosion current in the present study. The magnitude of the filiform
corrosion current for the present set of alloys is determined by a combination of observed
trends for the cathodic current in the catholyte and passive range under anolyte conditions
with variation of the particle distribution. The highest filiform corrosion current is derived
for the $\beta^+$-conditions and this tendency decreases with coarsening of the precipitate
distribution from the $\beta(1)$- to the $\beta(3)$-conditions.
For the alloys tested the filiform corrosion initiation characteristics are related to the
passive range and thus implicitly to the ease of pitting. A smaller passive range tends to
correlate with a higher filiform site density. The supposed correlation between the ease of
pitting and the ease of filiform corrosion initiation and propagation is best expressed by the
very clear trend of the increasing filiform corrosion current with the corrosion number.
In conclusion: the results of this thesis have shown that the susceptibility to filiform corrosion of aluminium alloys can be related to features of potentiodynamic polarisation measurements in synthetic electrolytes mimicking the anolyte and catholyte in the tip of the filament. The filiform corrosion current, defined as the intercept of the cathodic curve in the catholyte and the anodic curve in the anolyte, corresponds to the filiform corrosion propagation rate, provided that the cathodic reaction in the anolyte, i.e. the hydrogen reduction reaction, is not hampered. Furthermore it was found that the filiform corrosion initiation susceptibility correlates with the magnitude of the passive range under anolyte conditions and thus implicitly seems to be related to the ease of pitting of the alloy. A smaller passive range results in a higher filament site density for the alloys tested.
Samenvatting

Dit proefschrift beschrijft de resultaten van een aantal gecombineerde filiform corrosie en potentiodynamische polarisatiemetingen op een reeks van binaire en industriële legeringen teneinde het effect van microstructurele variaties in het substraat te verhelderen. In Hoofdstuk 1 wordt de huidige kennis met betrekking tot filiform corrosie, inclusief het effect van het substraat, oppervlaktebehandeling en organische coating, zoals beschreven in de literatuur samengevat en gestructureerd. Speciale aandacht wordt geschonken aan de electrochemische reacties die plaatsvinden aan het coating-substraat oppervlak.

Met versmelde filiform corrosie expositiesteen op elf binaire en een ternaire modellegering zoals beschreven in Hoofdstuk 2 worden de chemische samenstellings- en voorbehandelingseffecten op het filiform corrosiegedrag van de geteste substraten aangetoond en gekwantificeerd. Voor alle binaire legeringen welke slechts een ontvettingsbehandeling hadden gekregen voordat de organische coating werd aangebracht, nam de bezettingsgraad van de filamenten toe met toenemende concentratie van het legeringselement. Deze trend van een toenemende gemiddelde filamentlengte met de legeringsconcentratie is vooral duidelijk voor de zeer filiform corrosie gevoelige Al-Cu binaire legeringen, maar ook voor de Al-Si legeringen. Dit in tegenstelling tot de ontvette Al-Zn en Al-Mg legeringen welke geen of slechts een kleine significante toename in gemiddelde filamentlengte met de legeringsconcentratie laten zien. Analyse van de totale filiform corrosie-aantasting middels het corrosiegetal, gedefinieerd als het produkt van de bezettingsgraad en de gemiddelde filamentlengte, laat zien dat het gemiddelde corrosiegetal afneemt in de volgorde Al-Cu, Al-Si, Al-Zn en Al-Mg. Verdere analyse van de corrosiegetal data van het binaire legering systeem leert dat het corrosiegetal toeneemt met de legeringsconcentratie voor alle binaire legeringen. Bovenstaande waarnemingen onderbouwen de toepasbaarheid van de fundamentele oorzaak van lokale corrosieprocessen op filiform corrosie van aluminium legeringen. Opeenvolgende interacties tussen de legeringsmatrix en deeltjes worden beïnvloed door de legeringselementen en hun concentraties. De trend voor een toenemend corrosiegetal met de legeringsconcentratie is vooral duidelijk voor ontvette substraten. Op de gechromateerde en gecerateerde substraten was de filiform corrosie aantasting te gering om een dergelijke correlatie met enige statistische significantie te bevestigen, maar de data spreken een dergelijke correlatie ook
Samenvatting

niet tegen.
Hoewel de gedetailleerde analyse van de filiform corrosie snelheid als functie van de substraatsamenstelling en de oppervlaktebehandeling, zoals gepresenteerd in Hoofdstuk 2, waardevolle resultaten geeft, geeft het geen verklaring voor de waargenomen afhankelijkheden. De onderliggende filiform corrosie mechanismen kunnen alleen verder worden opgehelderd door het uitvoeren van electrochemische metingen in oplossingen welke karakteristiek zijn voor het bestudeerde corrosieproces. Hiertoe zijn de resultaten van potentiodynamische polarisatiemetingen in kunstmatige anolyt- en katholyt-oplossingen, welke karakteristiek zijn voor de lokale anodische en kathodische sites in de filamenten op aluminium substraten, gepresenteerd in Hoofdstuk 3. De potentiodynamische polarisatiemetingen zijn uitgevoerd op twee Al-Cu binaire legeringen en vier Al-Zn binaire legeringen. Een correlatie tussen de filiform corrosiestroom, gedefinieerd als het snijpunt van de kathodische curve in het katholyt en de anodische curve in het anolyt, en de gemiddelde filamentlengte na de versnelde expositiestroom test waargenomen voor de Al-Cu binaire legeringen. Een dergelijke correlatie is niet waargenomen voor de Al-Zn legeringen, waarbij een toename van de filiform corrosiestroom nauwelijks wordt weerspiegeld in een hogere gemiddelde filamentlengte. Wanneer de resultaten voor de Al-Cu en Al-Zn binaire legeringen worden vergeleken kan worden geconcludeerd dat de correlatie significant afhankt van het legeringselement en dat de gedefinieerde filiform corrosiestroom een niet-uniek onderscheidende parameter is voor de filiform corrosiegevoeligheid van de onderzochte set modelleren. De verschillende correlatiefactoren voor de Al-Cu en Al-Zn legeringen zijn te verklaren vanwege de electrochemische respons op lokale variaties van de substraatsamenstelling. De sterke relatie tussen de filiform corrosiestroom en de gemiddelde filamentlengte voor de Al-Cu binaire legeringen is gerelateerd aan de significante toename van de kathodische en anodische reactiesnelheid met toenemende Cu concentratie. De binaire Al-Zn legeringen laten een meer constant overall anodische en kathodische reactiesnelheid zien als functie van de Zn concentratie. Dit is het gevolg van een afnemende kathodische reactiesnelheid in het anolyt met toenemende Zn concentratie, ten gevolge van een afnemende waterstof reductiesnelheid, welke een toenemende filiform corrosiegroeisnelheid begrensd. Dit zou de toenemende gemiddelde filamentlengte met Cu concentratie en de meer constante gemiddelde filamentlengte met toenemende Zn concentratie na 1000 uur versnelde expositiestroom verklaren.
Voor de Al-Cu en Al-Zn modelleren correleert de filament bezettingsgraad met de
grootte van het passieve gebied in het anolyt en lijkt de filiform corrosie initiatie impliciet gerelateerd te zijn aan de gevoeligheid voor putvormige corrosie van de legering. Een klein passief gebied resulteert in een hogere filament bezettingsgraad voor zowel de Al-Cu als de Al-Zn legeringen.

In Hoofdstuk 4 wordt een mechanisme studee van filiform corrosie op AA2024-T351 gepresenteerd, met als doel het algemene en lokale mechanisme van filiform corrosie op aluminium legeringen op te helderen en te bevestigen. Het algemene mechanisme is herhaald middels Scanning Kelvin Probe metingen welke corrosiepotentiaal variaties in filamenten laat zien, waarmee het anodische ondernijning mechanisme voor filiform corrosie op aluminium legeringen kon worden afgeleid. De samenstelling van de electrolyt condities in de uiterste tip van het filament is bepaald en een kunstmatig anolyt is gedefinieerd. Dit anolyt en het ermee samenhangende katholyt zijn gebruikt in alle potentiodynamische polarisatiemetingen. Het anolyt wordt gekarakteriseerd door lage pH (pH waarden van 1-2 zijn gemeten) en een hoge chloride concentratie. De lokaal hoge chloride concentratie in de uiterste tip van echte filamenten is bevestigd door EDX analyse op proefstukken waarvan de organische coating is verwijderd. In-situ time lapse video waarnemingen laten de waterstofontwikkeling in de filament tip en een stapsgewijze propagatie van de filament tip zien. Dit stapsgewijze groeigedrag is gerelateerd aan de discontinue opslag van elastische energie in de organische coating en de ontlasting hiervan wanneer de hechtingssterkte wordt overschreden. In het geval reproduceerbaar, gelijke en goed hechtende coatings en voorbehandelingen worden toegepast, kunnen de verschillen in gemiddelde filiform corrosie propagatiesnelheden van gecoate substraten toegeschreven worden aan verschillen in de microstructuur van de substraten, met het stapsgewijze groeimechanisme als tweede-orde effect.

In Hoofdstuk 5 wordt de versterking van filiform corrosie door de aanwezigheid van (edele) macro-defecten onderzocht en bevestigd door filiform corrosietesten op modellsubstraten voorzien van kopervrij lijndefecten of koperen pennen in geboorde gaten. Uit de filiform corrosietesten op de AA2024-T351 substraten met de koperen pen als macro-defect kan worden geconcludeerd dat de filiform corrosie initiatie en propagatie direct naast het (edele) macro-defect wordt gestimuleerd. Meer en langere filamenten worden waargenomen ter plaatse van de koperen pen. Voor de ontvette proefstukken kon versterkte filiform corrosie initiatie in de aangrenzende kras niet bevestigd worden, maar het gedeoxideerde sample laat een significante toename zien van het aantal filamenten in de aangrenzende kras. De filiform corrosie propagatie in de aangrenzende kras wordt
gestimuleerd door de aanwezigheid van de koperen pen, hetgeen in lijn is met de waarnemingen voor modelsubstraten met koperrijke lijndefecten. Het zal duidelijk zijn dat de afstand die beïnvloed wordt door het macro-defect, in de vorm van koperrijk lijndefect of koperen pen, niet oneindig zal zijn maar wordt geschat voor de huidige proefstuk- en defecteconfiguraties in de orde van grootte van één of enkele centimeters. De waarnemingen laten zien dat relatieve lange afstandseffecten ten gevolge van de aanwezigheid van edele kunstmatige macro-defecten filiform corrosie stimuleren op een effectief vergelijkbare manier als de lokale effecten van edele intermetallische deeltjes.

Deze waarnemingen bevestigen impliciet het lokale substraataantastingsmodel zoals gepresenteerd in dit proefschrift. Het laat het belang zien van de aanwezigheid van kathodisch actieve fases (zoals de koperrijke (macro) fases voor de geteste modelsubstraten) met name aan het substraatoppervlak voor de filiform corrosie-aantasting, hetgeen volledig in lijn is met de waarnemingen zoals gepresenteerd voor de binaire modellegeringen. Wanneer dergelijke kathodische fases afwezig zijn wordt de kathodische reactie niet gestimuleerd en blijken de substraten minder gevoelig te zijn voor filiform corrosie. Voor ontvette modelsubstraten met magnesiumrijke lijndefecten initieerde de filiform corrosie, onafhankelijk van de magnesiumconcentratie aan het oppervlak niet ter plaatse van de magnesiumrijke lijndefecten. In het geval van aanwezigheid van anodische fases, zoals de magnesiumrijke macro fases, is snelle oplossing van de matrix niet voor de hand liggend. De anodische fases zullen preferentieel oplossen hetgeen een relatief homogeen substraatoppervlak tot gevolg heeft. In afwezigheid van edele heterogeniteiten in het substraatoppervlak zal lokale corrosie door de formatie van microgalvanische koppels niet optreden, hetgeen een relatief lage substraat aantastings snelheid tot gevolg heeft, ook niet erg afhankelijk van de concentratie van de anodische deeltjes.

Analyse van oppervlaktebehandelde AA2024-T351 proefstukken laat zien dat de filiform corrosie groeirichting voor gewalste oppervlakken preferentieel in de walsrichting is. Voor mechanisch oppervlaktebehandelde substraten is de preferentiële filiform corrosie groeirichting in de richting van het mechanisch schuren en polijsten. Ter verklaring van de preferentiële groeirichting worden twee nieuwe kwalitatieve modellen gepresenteerd gebaseerd op respectievelijk een chemisch en geometrisch mechanisme. De chemische verklaring van het effect van walsen, schuren en bewerken berust op het blootleggen en uitzijnen van deeltjes (in essentie precipitat, dispersoiden en constitueerde deeltjes) resulterend in een hogere concentratie en/of fijnere verdeling van deeltjes in de
bewerkingsrichting. Het daardoor toegenomen kathodisch oppervlak zal leiden tot snelle uitbreiding van het corrosiefront in deze richting en zodoende een relatief hogere filiform corrosie groeisnelheid ten opzichte van andere richtingen. Anderzijds kan vanuit de klassieke scheurtip propagatie theorie worden beredeneerd dat de 'scheurtip', in dit geval de filament tip, zal openen en groeien in de richting van de scherpe kerf (kleine hoek van inval) en dus in de wals- of schuurrecht, aannemende dat gelijke chemische substraatoppervlak condities en mechanische druk in de filament tip in alle richtingen heersen. De relatieve bijdragen van de chemische en geometrische effecten is nog onderwerp van verdere studie. Applicatie van specifieke oppervlaktepatronen op AA2024-T351 substraten laat zien dat dit een erg effectieve manier is om begrenzing van de filiform corrosie-aantasting binnen het gebied van het oppervlaktepatroon te realiseren.

Tenslotte worden in *Hoofdstuk 6* de resultaten van een studie naar de effecten van pre- en post-extrusie warmtebehandelingen op de filiform corrosiegevoeligheid van de twee veel gebruikte commerciële legeringen AA6063 en AA6005 beschreven. De warmtebehandelingen en het extruderen vonden plaats onder industriële omstandigheden. De coatings zijn aangebracht onder laboratorium omstandigheden. De resultaten laten zien dat vergroting van de Mg2Si precipitaatverdeling leidt tot een afname van de filiform corrosie gevoeligheid van de geteste substraten. De hoogste filiform corrosie gevoeligheid is verkregen voor de B'-condities en deze gevoeligheid neemt voor alle chemische voorbehandelingen af van de β(1)- naar de β(3)-condities. Dit effect van de microstructuur op bezettingsgraad, gemiddelde filamentlengte en resulterende corrosiegehalte is het grootst voor de post-extrusie warmtebehandelde proefstukken. De resultaten voor de pre-extrusie warmtebehandelingen laten veel kleinere, maar nog steeds significante, effecten zien. De afname in effect kan verklaard worden door het (gedeeltelijk) in oplossing gaan van de verschillende deeltjesverdelingen gedurende het extrusieproces, waardoor er min of meer gelijke metaalkundige structuren in het geëxtrudeerde materiaal verkregen wordt.

Voor de set van post-extrusie warmtebehandelde proefstukken is een correlatie waargenomen tussen de potentiodynamische polarisatiemetingen enerzijds en filiform corrosie propagatie en totale aantasting na de versnelde expositietest anderzijds. De waargenomen correlaties voor de geteste legeringen kunnen verklaard worden vanuit de electrochemische respons op lokale variaties van de substraatsamenstelling. Voor gelijke deeltjesvolumes zal een groot kathodisch oppervlak deelnemen in de oplossing van de matrix voor een fijne verdeling van kathodische deeltjes, in samenhang met de, kleine in absolute zin maar significante, aantasting in de diepe gedurende het corrosieproces. Het
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grote kathodisch oppervlak zal hierdoor leiden tot een grotere kathodische stroom, een snelle uitbreiding van het corrosiefront en dus een hoge filiform corrosie groeisnelheid. Een dergelijke toename van de filiform corrosie gevoeligheid manifesteert zich in een grotere filiform corrosiestroom. De grootte van de filiform corrosiestroom voor de huidige set legeringen wordt bepaald door een combinatie van waargenomen trends voor de kathodische stroom in het katholyt en passieve gebied onder anolyt condities met variatie van de deeltjesverdeling. De hoogste filiform corrosiestroom is verkregen voor de $\beta^+$-condities en deze neemt af met vergroting van de deeltjesverdeling van de $\beta(1)$- naar de $\beta(3)$-condities.

Voor de geteste legeringen zijn de filiform corrosie initiatie karakteristieken gerelateerd aan het passieve gebied en dus impliciet aan de gevoeligheid van de legeringen voor putvormige corrosie. Een klein passief gebied lijkt voor de geteste legeringen te correleren met een hogere filiform bezettingsgraad. De veronderstelde correlatie tussen de gevoeligheid voor putvormige corrosie en de gevoeligheid voor filiform corrosie initiatie en propagatie wordt het duidelijkst weergegeven door de sterke relatie tussen de filiform corrosiestroom met het corrosiegetal.

Concluderend: de resultaten van dit proefschrift laten zien dat de gevoeligheid van filiform corrosie van aluminiumlegeringen gerelateerd kan worden aan kenmerken van potentiodynamische polarisatiemetingen in kunstmatige electrolyten, karakteristiek voor het anolyt en katholyt in de tip van het filament. De filiform corrosiestroom, gedefinieerd als het snijpunt van de kathodische curve in het katholyt en de anodische curve in het anolyt, correleert met de filiform corrosie groeisnelheid, mits de kathodische reactie in het anolyt, in essentie de waterstof reductiereactie, niet belemmerd wordt. Verder is geconstateerd dat de filiform corrosie initiatiegevoeligheid correleert met de grootte van het passieve gebied onder anolyt condities en zodoende impliciet met de gevoeligheid voor putvormige corrosie van de legering. Een kleiner passief gebied resulteert voor de geteste legeringen in een hogere filament bezettingsgraad.
Dankwoord

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List of publications


(paper and lecture)


In preparation to be submitted:


The effect of mechanical surface treatments on the filiform corrosion pattern on AA2024-T351 alloys, J.M.C. MOL, J.H.W. DE WIT and S. VAN DER ZWAAG