The Role of Magnesium in the Electrochemical Behaviour of 5XXX Aluminium-Magnesium Alloys

Proefschrift

Ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus, prof. dr. ir. J.T. Fokkema,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen
op maandag 10 april 2006 om 15:30 uur

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This research was carried out under the project number MC6.98050 in the framework of the Strategic Research Program of the Netherlands Institute for Metals Research (NIMR) in the Netherlands.

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Somewhere, something incredible is waiting to be known.  
When you make the finding yourself  
you'll never forget it.  
Carl Sagan (1934 - 1996)
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Chapter 1

Introduction

1.1 General Introduction

The AA5XXX aluminium alloys are generally known for their excellent corrosion resistance. This particular property makes them widely popular for various applications involving corrosive environments. Nevertheless, these alloys can become susceptible to intergranular corrosion (IGC) attack and intergranular stress corrosion cracking (IGSCC) when exposed to temperatures ranging from 50°C to 200°C for extended periods of time. A combination of temperature and aggressive environment can potentially bring negative effects to these alloys during service conditions.

The AA5XXX series also offer an excellent combination of strength and formability due to the presence of magnesium as alloying element [1]. Consequently, there is a strong incentive to use alloys with higher magnesium concentrations. The AA5xxx series spans a wide range of magnesium contents. In addition when magnesium is added in combination with other elements (e.g. copper and zinc), greater improvements in strength can be achieved. Existing tempers for these alloys are designated according to the magnesium content and the desired resulting microstructure [2].

It is believed that alloys with relatively low magnesium contents such as AA5052 and AA5454 (2.5% and 2.75% Mg, respectively) are resistant to SCC and eventually not affected by exposure to the elevated temperatures [3]. In contrast, alloys with the magnesium contents exceeding about 3% may develop susceptible structures to SCC as a result of continuous heating or even after extended periods of times at room temperature. Al-Mg alloys are
commonly used in marine, rail and rigid packaging applications where potential sensitising conditions are not of significant concern. Nowadays, there is a growing use of these alloys for automotive and structural application where the alloys could face sensitising temperatures [4,5]. These new applications bring, as a consequence, sensitisation problems back as a major concern.

Susceptibility to intergranular attack or SCC is frequently associated with increased grain boundary precipitation of $\beta$-$\text{Al}_2\text{Mg}_2$ phases, with the greatest susceptibility associated with a continuous precipitation of such phase [6, 7]. However, Jones et al. [8] demonstrated that SCC occurs when the $\beta$-phase exists as a discrete network rather than as a continuous network along the grain boundary. The results presented also indicated the existence of an additional mechanism by which cracks propagate between particles. Many observations reported of a continuous array of $\beta$-phase were made with optical metallography of etched surfaces [7,9,10] while TEM micrographs of aluminium alloys showed micrographs with extensive strain fields [11]. Strain fields can cause individual particles to appear continuous if they are closely spaced. Consequently, sample preparation is suggested to be a very crucial step.

It is important to emphasize that there is no question that the presence of the $\beta$-phase at grain boundaries is an important factor in the SCC and intergranular corrosion process in 5XXX aluminum alloys. It is obvious that increasing magnesium concentration in the alloy and increasing aging times will cause the spacing between $\beta$-phase particles to decrease. However, the mechanism by which cracks propagate between the $\beta$-phase particles and the specific role of the $\beta$-phase remain an open question. Moreover, knowledge on the role that Mg plays in the intergranular corrosion and SCC process in Al-Mg alloys is yet to be clarified.

1.2 Research Aim

The aim of this thesis is to understand the role of magnesium in the intergranular corrosion process of commercial Al-Mg alloys. Within this context, this thesis will elucidate the magnesium behaviour on the metal surface and at grain boundaries proposing, at the same
time, a possible mechanism of initiation and propagation of the intergranular corrosion attack in the AA5XXX series.

1.3 Thesis Outline

In chapter 2, a general overview of the AA5XXX alloys is given. This chapter mainly focuses on information available in the scientific literature regarding composition, common applications and what is known about intergranular corrosion susceptibility of these alloys.

The metal surface is the most important parameter for any corrosion process and, at the same time, the first line of defence for the metal against corrosion attack. For a better understanding of the corrosion process in Al-Mg alloys, chapter 3 explores the oxide layer and its subsequent transformation in aqueous solutions as well as the effects that alloying elements have in the electrochemical behaviour of the oxide layer.

Chapter 4 focuses on the role of magnesium enrichment in Al-Mg alloys and its effect on the composition of the oxide layer as a function of moderate sensitisation temperatures. This chapter also describes the electrochemical behaviour of the enriched oxide layer and how this situation can be extrapolated to other aluminium alloys that contain Mg as a major or minor alloying element.

Chapter 5 and chapter 6 deal with the electrochemical behaviour of the bulk metal. Chapter 5 concentrates more on the influence that sensitising temperatures have on the microstructure of the alloy as well as the type of precipitation induced by the sensitisation. Chapter 6 has the generic goal of understanding the effect of Mg content in the Al-Mg alloy as a precursor for intergranular corrosion susceptibility. Determination of grain boundary enrichment and/or precipitation as a function of temperature and as function of Mg content is studied in this chapter. A model for the initiation and propagation of intergranular corrosion based on the electrochemical behaviour of magnesium and aluminium is introduced. Finally, general summary and topics for future research are presented.
1.4 References


Chapter 2

5XXX Aluminium Alloys

2.1 Importance of Mg in aluminium alloys

Addition of selected elements to pure aluminium greatly enhances its mechanical, physical, and chemical properties, extending its range of possible applications. For this reason, most applications for aluminium utilize alloys having one or more elemental additions. The major alloying additions used in aluminium are copper, manganese, silicon, magnesium and zinc.

Magnesium is an important element frequently used as a major (or minor) alloying addition in aluminium alloys. Magnesium is the lightest of all the structural metals with a density that is two thirds that of aluminium and one quarter that of iron [1]. By itself, magnesium is soft. However when added to aluminium, Mg provides substantial strengthening and improvement of the work hardening characteristics of aluminium. Magnesium is also added in combination with other elements, notably copper and zinc, for even greater improvements in strength [1, 4, 5].

Mg is an effective strengthener on a weight basis and has the added advantage to be highly soluble in aluminium [1, 4]. The amount of magnesium that can be retained in solid solution in commercial alloys is affected by the presence of other elements, mainly Si and Cu, which react with magnesium during cooling to form either Al(Cu,Mg) or Mg₂Si phases, lowering the solute content of the matrix [5].
2.2 Role of Mg in different aluminium alloys

The effects and benefits of adding Mg in aluminium alloys depend on the type of alloy (heat-treatable vs. non-heat treatable) and their thermo-mechanical processing. For instance, the addition of Mg to Al-Cu alloys enhances both the magnitude and the rate of natural aging [2]. This enhancement probably results from the complex interaction between Mg and Cu atoms in solid solution. The formation of the strengthening precipitates in these alloys is determined by the weight ratio of Cu and Mg. When Mg is added in Al-Cu alloys in concentrations higher than 1wt% then two strengthening phases will be formed coexisting in the alloy; these phases are: $\theta$-phase ($\text{Al}_2\text{Cu}$) and the S-phase ($\text{Al}_2\text{CuMg}$). The S-phase comprises 60% of the particles in the alloyed metal [3]. Moreover, the S-phase is identified as the principal strengthening phase in Al-Cu-Mg alloys [4]

A similar effect can be achieved when Mg is added in Al-Si alloys to form $\text{Mg}_2\text{Si}$ precipitate for strengthening. In this particular case, the ratio between Mg and Si is of great importance. Commercial alloys in the AA6XXX family can be divided in three groups [1, 5]. In the first group, balanced amount of Mg and Si are added to the alloy in the range of 0.8% and 1.2%. The AA6063 alloy represents a good example of this type of alloys. The second group consists of an amount of Mg and Si in excess of 1.4%. These alloys are more quench sensitive and develop higher strength on aging. Copper is usually added in the range of 0.25wt% to improve mechanical properties. The AA6061 is an example of this type of alloys. Finally, the third group of alloys consists of having Si in excess of that needed to form $\text{Mg}_2\text{Si}$, and as a consequence of this excess, Si promotes an additional response to age hardening but it may also result in loss of ductility as well as increases susceptibility to intergranular embrittlement due to Si segregation to grain boundaries. Examples of this group are AA6151 and AA6351.

When Mg is added to Al-Zn alloys, it provides an improved strength of this system especially in the range of 3 to 7.5wt% Zn. Magnesium and zinc form $\text{MgZn}_2$, which produces a far greater response to heat treatment than occurs in the binary Al-Zn system [4, 5]. The addition of magnesium in excess of that required to form $\text{MgZn}_2$ further increases tensile strength of the alloy. Moreover, Mg additions greatly reduce the low temperature solubility of Zn in Al [5].
5XXX aluminium alloys

The binary aluminium-magnesium system (Al-Mg) is the basis for the AA5XXX alloy series of non-heat-treatable aluminium alloys in which magnesium forms a complicated system with aluminium. Magnesium has a high solid solubility in aluminium at high temperatures (up to 14.9wt% at 450°C). Its solubility decreases to approximately 1.7wt% at room temperature but the rate of decomposition of the supersaturated solid solution is very low [1, 4]. In addition, magnesium decreases linearly the density of aluminium by approximately 0.5% for every 1wt%Mg in solid solution [6].

Mg content in commercial 5XXX alloys ranges from 0.5 to about 6wt%. Alloys with low Mg content (lower than 3.5wt% Mg) are used where formability or surface finishing are critical [6]. The good formability of Al-Mg alloys is attributable to the high strain-hardening rate. On the other hand, higher Mg content (higher than 3.5wt%) alloys are used in structural applications where strength, fracture and fatigue resistance, and weldability are important [6]. When the magnesium content in the Al-Mg system exceeds 3.5wt%, β-phase (Mg2Al3) particles can be precipitated by lower temperature thermal treatment or by slow cooling from elevated temperatures [7]. For example if the AA5086 alloy, which contains about 4wt% Mg, is cold-worked and heated in the range of 120°C to 180°C, a continuous network of Mg2Al3 can be precipitated at the grain boundaries [8, 9].

There are only a few binary wrought Al-Mg alloys such as AA5005 and AA5050 alloys. Most of the alloys in this series are mixed with other elements to enhance their mechanical properties. Most Al-Mg alloys contain some manganese (0.1wt% to 1.0wt%) and/or chromium (0.1wt% to 0.25wt%) as well as other minor alloying elements such as Fe, Si and Zn in concentrations of less than 1at%. Examples of Al-Mg alloys with additions of chromium are AA5052 and AA5154, while AA5056, AA5083, AA5086, AA5454, and AA5456 are examples of alloys, which contain both manganese and chromium.

2.3 Chemical composition of representative AA5XXX alloys

Typical compositions of most representative alloys in the AA5XXX series are displayed in Table 2.1. Cu, Zn and Mn are very important minor additions in the Al-Mg alloys. Cu additions to Al-7%Mg alloys induce response to age hardening, but result in severe solute
Chapter 2

segregation problems [10]. Zn additions to Al-Mg alloys can result in strengthening through the precipitation of a τ-phase (Al$_2$Mg$_3$Zn$_3$) [11]. Mn is often added to 5XXX alloys to further strengthen the alloy at lower Mg levels. Relatively small additions of Mn to a 3.5%Mg binary can be more efficient in promoting strengthening than further Mg additions [5]. At higher levels, Mn precipitates as a dispersoid (Al$_6$Mn). On the other hand, chromium is a common addition in this type of alloys in which it is added in amounts not exceeding 0.35wt%. If the amount is higher than this limit, Cr tends to form very coarse constituents with other impurities or additions such as manganese and iron. Chromium is used to control grain structure, to prevent grain growth in aluminium magnesium alloys and to prevent recrystallization in Al-Mg-Si and Al-Mg-Zn alloys during hot working or heat treatment [5].

Table 2.1. Composition limits (wt%) of representative 5XXX aluminium alloys [12, 13]

<table>
<thead>
<tr>
<th></th>
<th>AA5040</th>
<th>AA5154</th>
<th>AA5454</th>
<th>AA5954</th>
<th>AA5356</th>
<th>AA5083</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.30</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>0.7</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Cu</td>
<td>0.25</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Mn</td>
<td>0.9-1.4</td>
<td>0.10</td>
<td>0.50-1.0</td>
<td>0.10</td>
<td>0.05-0.2</td>
<td>0.40-1.0</td>
</tr>
<tr>
<td>Mg</td>
<td>1.0-1.5</td>
<td>3.1-3.9</td>
<td>2.4-3.0</td>
<td>3.3-4.1</td>
<td>4.5-5.5</td>
<td>4.0-4.9</td>
</tr>
<tr>
<td>Cr</td>
<td>0.10-0.3</td>
<td>0.15-0.35</td>
<td>0.05-0.20</td>
<td>0.10</td>
<td>0.05-0.2</td>
<td>0.05-0.25</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25</td>
<td>0.20</td>
<td>0.25</td>
<td>0.2</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>Al</td>
<td>bal</td>
<td>Bal</td>
<td>Bal</td>
<td>bal</td>
<td>bal</td>
<td>bal</td>
</tr>
</tbody>
</table>

In the 5XXX series, AA5083 and AA5454 are the most representative alloys often called structural alloys. They are characterized by having the highest strength in the Al-Mg alloys family. In addition, they represent the two main groups in the 5XXX series in terms of corrosion properties: the corrosion resistant AA5454 with Mg content below 3.5% and the corrosion susceptible AA5083 with Mg content higher than 3.5%. AA5454 contains typically 2.7%Mg, 0.8%Mn, and 0.12%Cr and, according to some engineering specifications, it has the highest Mg content suitable for sustained elevated temperatures. In other words exposure to prolonged elevated temperatures, the alloy will develop only minimal precipitation at the grain boundaries [14]. AA5454 possesses the same properties as AA5083 alloy with
5XXX aluminium alloys

4.5%Mg. AA5083 is the most widely used alloy in the 5XXX series [12, 15]. It contains typically 4.5%Mg, 0.4%Mn, 0.1%Cr and it has a highly supersaturated Mg content. According to some engineering specification, it is relatively free of precipitates on grain boundaries (non-continuous paths) and therefore the material is not susceptible to stress corrosion cracking [15]. However, prolonged low temperature heating will induce continuous precipitates along the grain boundary, which results in susceptibility to stress corrosion cracking [15].

2.4 Precipitates in the AA5XXX alloy series

The precipitated particles in the AA5XXX alloys can be of various types, depending on the specific composition of the alloy. As previously mentioned, magnesium preferentially precipitates at grain boundaries as β-phase (\( \text{Al}_3\text{Mg}_2 \)) or (\( \text{Al}_8\text{Mg}_5 \)) [16]. In addition, due to the very low solubility of Si in aluminium at high Mg contents, Mg\(_2\)Si-precipitate is often present in the microstructure as a major constituent phase. The presence of Mg\(_2\)Si has a deleterious effect on ductility, fracture resistance, and most types of forming behaviour. The existence of Fe, Mn, and Si in the Al-Mg alloys induce precipitation in the form of Al\(_{12}\)(Fe,Mn)\(_3\)Si, Al\(_6\)(Fe,Mn), and/or Al\(_3\)Fe. When Mn precipitates as a dispersoid during preheating, the Al\(_6\)(Mn,Fe) phase is favoured since the Si is consumed by Mg\(_2\)Si. This dispersoid retards recrystallization and hence greatly enhances the rate of work hardening. The optimum dispersion of Al\(_6\)Mn occurs at a Mg content of 4.5wt% and a Mn content of 2wt% [17, 18]. Cr has a very low solubility in aluminium. During solidification and preheating, ternary compounds of Al, Mn, and Cr can form in alloys containing both Cr and Mn. In wrought sheet products, Cr is often present as Al\(_{12}\)Mg\(_2\)Cr as a result of precipitation during the pre-heat [19]. However, Cr may be retained in solid solution due to its low diffusivity in aluminium or precipitated as binary Al-Cr phase, depending upon exact alloy composition and process conditions.

2.5 Typical Application of 5XXX aluminium alloys

Table 2.2 summarizes some typical application of 5XXX aluminium alloys. Applications of these alloys range from welding applications (weld fillers) and truck bodies to construction of tactical military vehicles. For example, the hulls and turrets of vehicles such as the M113
armoured personnel carrier, the M2/M3 infantry and cavalry fighting vehicles, the M109 self-propelled howitzer, and the AAV74 amphibians all consists of welded AA5083 aluminium structures.

Table 2. Typical applications of selected 5XXX aluminium alloys [20, 21]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Application description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5005 (0.8%Mg)</td>
<td>Appliances, architectural, electrical conductors</td>
</tr>
<tr>
<td>AA5052 (0.25%Mg)</td>
<td>Sheet metal work, hydraulic tube, appliances</td>
</tr>
<tr>
<td>AA5056 (5.1%Mg)</td>
<td>Cable sheathing, rivets for magnesium alloys, screen wire, zippers</td>
</tr>
<tr>
<td>AA5083 (4.5%Mg) and AA5086 (4%Mg)</td>
<td>Welded pressure vessels, marine, auto aircraft cryogenics, TV towers, drilling rigs, transportation equipment, missile components</td>
</tr>
<tr>
<td>AA5154 (3.5%Mg)</td>
<td>Welded structure, storage tanks, pressure vessels, salt water service</td>
</tr>
<tr>
<td>AA5182 (5%Mg) and AA5252 (2.5%Mg)</td>
<td>Automobile body sheets, can ends</td>
</tr>
<tr>
<td>AA5454 (2.7%Mg)</td>
<td>Welding electrodes, welded structures, storage tanks for heated products, pressure vessels, truck bodies for hot oil or asphalt applications</td>
</tr>
<tr>
<td>AA5456 (5.1%Mg)</td>
<td>High strength welded structures, storage tanks, pressure vessels, marine applications</td>
</tr>
<tr>
<td>AA5652 (2.7%Mg)</td>
<td>Hydrogen peroxide and chemical storage vessels</td>
</tr>
</tbody>
</table>

2.6 Intergranular Corrosion of 5XXX Aluminium Alloys

Intergranular corrosion (IGC) is a localized type of corrosion that occurs at and near the grain boundaries with relatively little corrosion in the grain interiors. Each of these metal grains has a clearly defined boundary that, in most cases, chemically differs from the metal within the grain center. Intergranular corrosion can be associated with several factors such as segregation of impurities at the grain boundaries, enrichment or depletion of one or more of the alloying elements on the grain boundary area [12]. In addition, the existence of precipitates in the form of dispersoids, coarse particles, strengthening phases and impurities with chemistries so different from the rest of the matrix can induce electrochemical reactions in the form of localized corrosion [22]. Under a specific environment, these electrochemical reactions can induce grains to fall apart disintegrating the metal or just decreasing the
cohesive strength between grains. This situation can appear in the visual form of exfoliation or in the less evident form of stress corrosion cracking. Nevertheless, improvements in the localized corrosion resistance of aluminium by conventional alloying techniques are limited by mainly two factors. First of all, alloying techniques are normally based on strength considerations. In other words, they are intended to improve the mechanical properties of the alloyed metal rather than improving its corrosion resistance. Secondly, most alloying elements known to impart improved corrosion properties have a limited solubility in aluminium.

Several studies have been performed on the AA5XXX series regarding its corrosion behaviour in aggressive media, mainly on 5083 (4.5wt% Mg) [23, 24, 25]. When the magnesium content in Al-Mg alloys exceeds about 3-4wt%, β-phase (Mg2Al3) can be precipitated by lower temperature thermal treatments or by slow cooling from elevated temperatures. For example if the 5086 alloy, which contains about 4wt% Mg, is cold-worked and heated in the 120 to 180\(^\circ\)C range, a continuous network of Mg2Al3 can be precipitated at grain boundaries [26, 27]. These precipitates on the grain boundaries can make the alloy susceptible to SCC under aggressive media conditions, and in the best case, they might be a source for pitting corrosion.

Al-Mg alloys containing less than 3wt% Mg are reported to be quite resistant to intergranular corrosion. In unusual cases, intergranular attack has occurred in these alloys on the welding heat-affected zones after months or years of exposure to moderately elevated temperatures in hot acidified ammonium nitrate aqueous solutions or just hot potable water [28]. On the other hand, alloys with high magnesium concentration can become susceptible to IGC due to precipitation of the Mg2Al3 phase. The degree of susceptibility increases with magnesium content, time of exposure to elevated temperatures and amount of cold work [29,30].

2.7 Summary
Magnesium is an important element frequently used as a major (or minor) alloying addition in aluminium alloys. Magnesium is an effective strengthener on a weight basis and has the added advantage to be highly soluble in aluminium. The amount of magnesium that can be retained in solid solution in commercial alloys is affected by the presence of other elements,
mainly Si and Cu, which react with magnesium during cooling to form either Al(Cu,Mg) or Mg$_2$Si phases, lowering the solute content of the matrix. Numerous tempers have been developed to improve the mechanical properties of the Al-Mg alloys. However, few of these tempers are designed to improve the corrosion properties of these alloys by controlling the size, amount and location of precipitates. There are several examples of alloys thought to be resistant to intergranular corrosion or stress corrosion cracking that have suffered failure during service conditions. This situation shows that initiation of IGC attack is more complex than previously suggested. However, the correlation between intermetallics and IGC is not yet completely understood. In order to develop a more accurate description of IGC attack in AA5XXX alloys, it is necessary to include the effects of other factors such as the enrichment of alloying elements on the grain boundaries and surface.

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5XXX aluminium alloys


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Chapter 3

Formation and Transformation of the Aluminium Oxide Layer in Air and Aqueous Solutions

3.1 Introduction

Aluminium alloys are widely used because of their lightweight, high strength, and good corrosion resistance. Aluminium, being inherently an active metal, owes its stability to the formation of a protective oxide film. This amorphous oxide film (natural oxide) formed on the bare aluminium surface provides good corrosion resistance in most natural atmospheres, seawater, fresh water, as well as in many soils and chemicals [1]. In addition, aluminium oxide films have an extensive range of applications in microelectronic devices as dielectrics diffusion and/or tunnelling barrier [2,3] because of its specific physical and chemical properties (i.e. large dielectric constant (~10), large barrier height for electric tunnelling, good thermal and mechanical stability, good adhesion). In order to better understand the corrosion process that aluminium and its alloys suffer, it is necessary to understand the properties of the oxide film, its formation in air and the transformation that this film experiences in the presence of an aqueous solution.

3.2 Formation of the oxide layer in air

The chemical composition, morphology, and microstructure of an oxide film formed on aluminium have a direct influence on a variety of important properties such as friction, adhesion and dielectric capacity. The oxide film formation and growth process requires that the metal and oxygen species dissolve in and move through the developing oxide film. Although the oxide formation at room temperature has some differences compared to the
oxide formation at temperatures above 300°C, it is generally agreed [4-7] that the formation mechanism can be summarized as follow.

The initial and subsequent stages of oxide formation comprises a series of steps such as arrival of oxygen molecules and subsequent dissociative-chemisorption on to the metal surface, nucleation and growth of the oxide film covering the metal surface including the transport of metal ionic species as well as electronic species (overall charge neutrality has to be maintained).

In general, the initial formation of the oxide is suggested to proceed by a so-called “island by layer growth” mechanism [4, 5], involving the lateral diffusion of mobile oxygen species over the aluminium surface (Figure 3.1). In other words, the growth will change from layer to island after one or two monolayers of the oxide are on the surface due to a change in surface energy (Figure 3.2). During the first few seconds, the metal is covered with a uniform oxide of 2 or 3 monolayers thick [4, 6].

![Figure 3-1. Initial aluminium oxidation diagram. The process involves the flux of metal cations (Al$^{3+}$), flux of metal vacancies (V$_{M}$), flux of electrons (e$^{-}$) and holes (h).](image)

At room temperature, it is generally assumed that no net electric charge is transported through the oxide and no space charge is built up in the oxide film. This assertion comes as a result of thinking that the thermal energy is insufficient to allow existing ions or electrons to surmount the energy barrier, calculated to be approximately 2.5 to 4.5eV [7,8,9]. Therefore, the driving
force postulated to account for the initially very fast oxidation rates observed is an electric field [10, 11, 12].

![Diagram of island-by-layer growth mechanism](image)

**Island**

**Bulk Metal**

**Aluminum oxygen bond (Al-O)**

**Metal vacancies**

Figure 3-2. Island-by-layer growth mechanism occurring in the formation and growth of the aluminium oxide layer. In metal deficient oxides, the main type of defects is the formation of metal vacancies.

In fact, Jeurgens et al. [13] established that during the oxidation of the metal a series of steps (one of these steps much slower than the rest, it may be the limiting factor in the oxide growth rate) are involved:

- Arrival of oxygen molecules (from gas phase)
- Dissociative chemisorption on to the metal surface
- Nucleation and growth of an oxide film
- Transport of ionic and electronic species from the oxide film to the oxide/air and metal/oxide interface.

During the oxidation process, a direct balance between the flux of ionic and electronic species is established in such way that the rate-limiting step proceeds at the maximum possible rate. If the transport of one of the concerned charged species through the oxide film occurs intrinsically at a relative faster rate, then an electric field will be set up within the oxide film. The direction of the field will be such that the transport of the less mobile rate-limiting species is enhanced.
At temperatures below 300°C, the oxide film exhibits a deficiency of Al cations as compared to a crystalline oxide. The Al cation concentration increases with increasing temperature and oxidation time. On the basis of cations deficiency, it is concluded that at room temperature the oxide growth rate during the initial fast oxidation stage is governed by the electric field enhanced outward migration of Al cations across the developing oxide film and electron tunnelling [14]. A logarithmic-type oxide film growth kinetics is usually followed in this case. That is, the initial fast-oxide fast-growth regime is followed by a transition to a slower growth regime ending up with an amorphous oxide layer of limited thickness in the range of 0.5 to 8nm. At the end of this stage of fast oxidation, the electron tunnel current has become effectively zero because of the formation of a rate-limiting barrier for Al cation’s motion. As previously mentioned, the barrier is estimated to be 2.5 to 4.5eV, located at the metal/oxide interface. Then, under the constrain of coupled currents of electrons and cations, the oxide growth stops because the chemical diffusion of ions across the oxide film as well as the contribution of electron transport by thermoionic emission are negligible. Thus, the oxide film growth culminates with an Al deficient amorphous oxide layer of limiting thickness.

In contrast, the oxide formation at T ≥ 300°C has the following characteristics [13]:

- Thermal energy is sufficient to surmount the barrier (for ions and electrons)
- Diffusion of ionic species into and through the developing oxide film under the influence of a concentration gradient (chemical potential)
- Transport of electrons through the developing oxide film by both tunnelling and thermoionic emission of electrons from the Fermi level of the metal into the conduction band of the oxide.

The main driving force at these temperatures is the concentration gradient (i.e. chemical potential) across the oxide layer building relatively thick oxide films (>10nm) [13]. Aluminium cation concentration increases with increasing temperature. During the initial oxidation at high temperatures, an aluminium enriched amorphous oxide is formed which gradually becomes crystalline. From this point, we will only refer to oxide films formed at temperatures below 300°C.
3.3 Transformation of the oxide by the presence of alloying elements.

The mechanical, physical and chemical properties of aluminium alloys depend on composition and microstructure. The addition of selected elements to pure aluminium greatly enhances its properties and usefulness. Most applications of aluminium utilize alloys having one or more elemental additions. The major alloying additions used with aluminium are copper, manganese, magnesium, silicon, and zinc; other elements are added in small amounts for grain refinement and to develop special properties. Total amount of these elements can constitute up to 10% of the alloy composition. Impurity elements are also present but they constitute usually less than 0.15% in the aluminium alloy [15, 16].

Alloying elements are found to segregate into the oxide layer during the low temperature oxidation process. Evidently during the hot rolling process, the alloyed metal is subjected to temperatures above 300°C that induce alloy segregation to the surface by a thermomigration process. Therefore, it is expected to observe some enrichment of alloying elements in the oxide of the final rolled product. However, at room temperature there is still a small contribution of (selective) alloying elements in the formation of the oxide film.

Nonetheless, the same process already described for aluminium governs the segregation of alloying elements into the oxide layer. In other words, the main driving force still is the formation of an electric field. The direction of the field will be such that the transport of the less mobile rate limiting species is enhanced. This idea is supported by the work of Macdonald [17]. He found that for the segregation of elements in the oxide film, the most highly charged species are the most strongly segregated species in the film whereas the least charged are the least segregated. In addition, when two species have the same charge then the lowest activation energy is the main factor influencing the segregation.

In an aluminium alloy, one can find several alloying elements that give aluminium all those widely popular properties such as strength, hardness, and corrosion resistance. For the sake of argument, it would be illustrated this segregation effect with the following example: we have selected iron (Fe), copper (Cu), zinc (Zn), magnesium (Mg) and manganese (Mn) for this example since they represent the most frequently alloying elements employed in commercial aluminium alloys.
As already mentioned during the oxide formation at room temperature, the oxide layer will be formed mainly as an amorphous aluminium oxide. According to Macdonald’s statement, in the presence of an electric field, alloying elements will be segregated into the oxide layer to the following extent:

- The most highly charged species are the most strongly segregated:
  \[ \text{Mg}^{2+} = \text{Cu}^{2+} = \text{Zn}^{2+} = \text{Mn}^{2+} = \text{Fe}^{2+} < \text{Al}^{3+} \]

- When two or more species have the same charge then the lowest activation energy is the main factor influencing the segregation. Hence, the elements arranged in terms of their activation energy are as follow:
  \[ \text{Mg} < \text{Zn} < \text{Cu} < \text{Mn} < \text{Fe} \]

The electric field favours the species with the highest charge (i.e. Al\(^{3+}\)). Obviously, aluminium cations are the main species involved in the formation of the oxide. In the case of alloying elements present in the bulk metal, most of the species have the same charge. For this reason, we apply the second statement concentrating the attention to the activation energies. In this case, it is found that magnesium has the lowest activation energy (\(\Delta Q = 30\) kJ/mol [18]), whereas iron has the highest (\(\Delta Q = 163\) kJ/mol [19]). Based on this analysis and under room temperature conditions, Mg and Zn should be incorporated in the oxide film. However, magnesium is the only element found to contribute in a minor way to the formation of the oxide layer at room temperature. In general, beside cation charge, alloy segregation to the oxide layer will also depend on temperature, concentration of the alloying elements in the bulk metal, as well as mobility of the alloying elements in the aluminium oxide layer.

Alloy enrichment has also been reported to occur during anodic oxidation (anodizing) of aluminium alloys [20, 21]. In this case, Habazaki et al. established that the amount of enrichment is directly proportional to the Gibbs free energy per equivalent of formation of the alloying element oxide [21]. In other words, the alloy enrichment increases as the Gibbs free energy of oxide formation per equivalent of each alloying element increases, as it can be seen in Figure 3-3. This situation is in agreement with the model of Macdonald.
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Figure 3-3. Linear relation between the enrichment of the alloy and the Gibbs free energy of oxide formation per equivalent of the alloying element oxide (Gibbs free energy of formation of bulk crystalline oxides) [21]

3.4 Transformation of the oxide layer by the presence of second phase intermetallics

Aluminium strength is commonly increased by the hardening process obtained by alloying aluminium with several elements such as Cu, Mg, Mn, etc. The addition of alloying elements to pure metals may alter the dimension or configuration of their lattice structures, turning the space lattice very complex. The wide variety of precipitate phases in aluminium alloys has been the subject of considerable study [22]. Precipitation affects not only mechanical properties but also physical properties (e.g. density, electrical and thermal conductivities) and electrochemical properties.

On the submicroscopic scales, the existence of intermetallics on the metal surface (precipitates, dispersoids, constituent phases, etc.) induces an abnormal oxide growth not yet well understood. Since intermetallics have a different chemical composition from the bulk metal, it is expected that they will induce changes on the composition as well as on the morphology of the oxide layer as illustrated in Figure 3-4. In addition, it is well documented that localized corrosion attack in the form of pitting in aluminium alloys starts 95% of the
times where intermetallics are located [23,24,25,26,27]. This situation indicates that the protective oxide layer is defective on these locations as shown in Figure 3-5.

There are two factors that support this hypothesis: First, the chemical composition of the intermetallic is like having an entirely new micro-alloyed metal in which its surface is rough and (probably) highly inhomogeneous. These features probably will induce stresses or other type of defects in the oxide structure during the growth of the oxide film. Second, the chemical composition of the precipitate can induce enrichment of one or more elements (precipitate’s alloying elements) in the oxide layer modifying its physical and electrochemical properties (corrosion resistance) of the film. The selection of which elements will segregate preferentially to the oxide as well as the extent of the segregation will depend, among other factors, on the charge of the species as well as their activation energy; concentration of the alloys in the bulk metal, temperature of the surroundings, and mobility of charge species in the oxide layer (diffusion properties) are also crucial in this case.

Figure 3-4. Effects that precipitates have on the oxide growth on aluminium alloys
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Figure 3-5. Localized corrosion in the form of pitting attack caused by intermetallics: a) AA2024 and b) AA5454, both immersed in 0.65M (mole/litre) sodium chloride (NaCl) for 5 days.

The idea of enrichment by intermetallics is supported by the work of Shimizu et al. [28, 29]. They showed how precipitates influence the growth of anodic aluminium oxide films, mainly in two ways: First, the oxide grown on top of a precipitate have a distinctive texture compared to the oxide formed on the surrounding aluminium matrix. For instance, Al₆Fe precipitates induce a finer and more porous texture oxide film whereas the oxide layer formed on the aluminium matrix has a more compact structure [28]. A similar effect is reported for copper-rich precipitates [29]. Second, one or more elements of the precipitate’s composition are incorporated in the oxide layer, mainly in the particle/film interface. For example, the Al₆Fe particle induces the formation of an iron-rich layer of 1-5nm thick located right on the particle/film interface [28]. In the case of oxide enrichment caused by precipitates at room temperature and under normal conditions, the extent of enrichment is believed to be less marked than the enrichment obtained under anodizing conditions. It is expected that the area enriched would be no more than 2nm thick.

3.5 Transformation of the oxide layer in the presence of aqueous solutions

In aqueous solutions, the aluminium oxide layer remains amorphous but its structure undergoes a transformation into a bilayer film. In other words, the oxide transforms into a highly hydrated outer layer combined with an aluminium (amorphous) oxide barrier layer located at the metal/outer layer interface (Figure 3-6) [30, 31]. This oxide layer actively interacts with the solution environment; it grows, transforms and incorporates solute ions.
These stages are certainly dependant upon the composition and structure of the original oxide film. As mentioned before, the structural characteristics of the oxide depend on the material composition, the presence of micro-defects as well as macro-defects (inclusions, second phase particles, size, shape and composition). All these factors will influence the behaviour of the oxide layer in aqueous solutions. What is more, the composition of the aqueous solution also has a strong influence on the behaviour and transformation of the oxide film [32]. Among several key parameters, the solution pH has one of the largest influences on several processes both at the interface and interphase level. Specifically, pH affects the dissolution of aluminium and its oxide film, the adsorption of species on the passive film, and the surface charge of the oxide [33].

As a general rule, the protective aluminium oxide film is stable in aqueous solutions in the pH range of 4.0 to 9.0 [34]. Usually, the oxide film is readily soluble in strong acid and alkalis. However, in certain acid and alkaline solutions, aluminium is highly resistant to corrosion attack (Figure 3-7). For example, aluminium is immune in acetic acid, concentrated nitric acid, sodium disilicate, and concentrated ammonium hydroxide, which provide low and high pH conditions, respectively [35]. This example clearly illustrates that stability or instability of the protective layer cannot be determined solely by pH because the nature of the individual ions in the solution as well as their concentration can be the main controlling factor. In fact Hoar [36] established that adsorption is the primary act in every heterogeneous process at the metal/solution interface, and the nature of the adsorbed species determines whether the metal dissolves or reaches passivity.

It is believed that the passive film is thin and highly porous in strong acids (pH<3.5) and alkaline (pH>11.5) solutions. In these pH ranges neither the passive film nor the aluminium base metal are stable. These conditions provide a dynamic oxide film in terms of growing and dissolving simultaneously. In this case, the rate of dissolution is higher than the rate of oxide formation. In the stability region (4≤pH≤10), the rate of oxide growth exceeds that of dissolution resulting in a thicker oxide film and less porous. In this case, the passive film is stable, efficiently retarding the interaction between the electrolyte and the bulk metal.
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Figure 3-6. Schematic of the processes that lead to the formation of bilayer passive films on metal surfaces.

Figure 3-7. Aluminium dissolution rate as a function of pH for different acids and alkaline solutions [35].

Besides the rate of formation and dissolution of the oxide film, redeposition on the surface during the oxide layer growth indicates that ionic solubility near the metal surface plays also an important role. In strong acidic and alkaline solutions, the aluminium concentration in the aqueous solution is significantly below the solubility limit of aluminium ions; consequently,
no precipitation is expected. In the passive range ($4 \leq \text{pH} \leq 10$), the solubility of aluminium is very low. However, the passive film strongly and efficiently retards the introduction of aluminium ions into the solution. The local aluminium concentration near the surface can be so high that at a given pH (within the passive range), the dissolved aluminium will redeposit on the surface. This redeposition (precipitation in the electrochemical sense) most likely proceeds through a heterogeneous nucleation. This heterogeneous process can be initiated by adsorption of hydrolyzed aluminium ions at the oxide/solution interface [37, 38].

Due to this partially hydrolysis process, the surface of the metal mainly the outermost part of the bilayer structure, suffers an additional transformation. That is, the outer-layer/solution interface is covered with a layer of hydroxyl groups [37, 38, 39]. The acid-base properties of the hydroxyl groups on the oxide film determine the surface charge of the oxide film when immersed in an aqueous solution. This surface charge on the oxide layer is important in its interaction with a charged species such as chloride, fluoride, bromide and iodine ions. An important parameter controlling the surface charge, and therefore, the characteristics of an oxide-covered metal is the pH of zero charge ($\text{pH}_{\text{pzc}}$) [40, 41]. The pH of zero charge ($\text{pH}_{\text{pzc}}$) of an oxide is the pH at which the surface of the oxide has no net charge [42]. At pH’s lower than the $\text{pH}_{\text{pzc}}$ the surface has a net positive character, and anions such as chloride ($\text{Cl}^-$) are electrostatically attracted to the surface and can be adsorbed into the oxide layer [41, 43]. The positive character of the surface can be represented as:

\[-\text{MOH}_{\text{surf}} + H^+_\text{aq} \leftrightarrow -\text{MOH}^+_{2\text{surf}},\]

where M represents the aluminium cation.

In contrast, when the pH is higher than the $\text{pH}_{\text{pzc}}$, the surface has a net negative charge and cations such as sodium ($\text{Na}^+$) from the solution are attracted to the surface [41, 43, 42]. The negative characteristic of the surface can be also represented as:

\[-\text{MOH}_{\text{surf}} + \text{OH}^- \leftrightarrow -\text{MO}^-_{\text{surf}} + H_2O, \text{ or}\]

\[-\text{MOH}_{\text{surf}} \leftrightarrow -\text{MO}^-_{\text{surf}} + H^+_\text{aq}\]

In the absence of polarization (induced electric field), the $\text{pH}_{\text{pzc}}$ will determine whether the oxide-covered surface has an acidic or basic character (in terms of Lewis acid-base definition
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[43, 44]) as illustrated in Figure 8, and determine the type of interaction with the solution ions will be.

The interaction of chloride ions with aluminium oxide layer in terms of the pH_{pzc} was clearly demonstrated by Kolics et al. [34, 45]. They suggested that there are two main mechanisms involve in the chloride-surface interaction of an aluminium metal immersed in 0.1M NaCl solution: First, the electrostatic attraction of chloride ions (Cl\(^-\)) to the oxide layer due to the positive characteristics of the surface charge (pH<pH_{pzc} = 9.1) and the attraction of sodium ions (Na\(^+\)) due to the negative characteristic of the surface charge (pH_{pzc}<pH) as shown in Figure 3-9. Second, the chloride deposition on the passive film is not restricted to the adsorption on surface hydroxyl groups. In other words, it is likely that part of the chloride ions penetrate the passive film through oxygen vacancies. This is an acceptable hypothesis since the radius of the chloride ion is slightly larger than that of an oxygen ion (1.81Å vs. 1.37Å, respectively), so that chloride migration through oxygen vacancies is a possible mechanism of chloride entry into the oxide layer [46, 47]. The penetration of Cl\(^-\) ions into the oxide layer has been demonstrated by Yu et al. [48]. Nonetheless, there are other interesting theories in the scientific literature that provide a plausible mechanism for chloride penetration as well. At the moment, a unified theory has not been yet achieved.
Figure 3-9. Interaction of a) chloride and b) sodium ions on the aluminium oxide film as function of pH. The aluminium surface was immersed in 0.1M NaCl for 45 minutes [45]

3.6 Influence of alloying elements and intermetallics on the oxide layer in the presence of an aqueous solution

The major corrosion problem with aluminium is the localized breakdown of the passive film, which leads to the initiation and growth of pits or initiation of intergranular corrosion. Improvements in the localized corrosion resistance of aluminium by conventional alloying techniques are limited by two considerations. First, selection and concentration of alloying elements are normally based on strength considerations, but the resulting precipitate phases normally alter the protective oxide disrupting the corrosion resistance capabilities. Second, most alloying elements known to offer improved corrosion properties have a limited incorporation to the aluminium solid solution [35, 49]
As mentioned previously, alloying elements can contribute to the formation of the oxide layer modifying its composition and, thus, its interaction with the aqueous media. Figure 8 illustrates how the composition (SiO$_2$ vs. Al$_2$O$_3$) of the oxide layer influences the value of the pH$_{pzc}$, the surface charge characteristics of the film and consequently, its interaction with the aqueous solution. This situation was demonstrated by Brockris [50], Natishan [51, 52] and McCafferty [53] by modifying the composition of the aluminium oxide with different elements such as Si, Ti, Cr, W, Mo and Zr. They observed that these elements modify the pH$_{pzc}$ to lower values as well as providing more positive pitting potentials than aluminium. There are some other elements (e.g. Mg, Li, Zn) that because of their nature will make the aluminium oxide to be more reactive to an aqueous media modifying the pH$_{pzc}$ to higher values.

In general, the effects that segregation of alloying elements have on the aluminium oxide layer can be: expansion or contraction of the passive range, formation of a compact or porous surface oxide, enhancement or detriment of resistance to localized breakdown of the passive films. Additionally, the extent of enrichment of the alloying elements in the oxide film will strongly depend on other factors such as the near-surface composition (ability of the alloying elements to move to the outer part of oxide layer), the electrochemical behavior of the metal/solution interface, and nature of the corrosion attack.

Intermetallics negatively affect the electrochemical properties of the oxide layer. These negative effects are more evident when the metal is exposed to an aqueous medium. Intermetallics induce the formation of defects as well as composition changes on the oxide layer, which eventually make difficult the growth of a protective layer. These weak points in the oxide are the origin of localized corrosion. In these points the corrosion attack proceeds with a higher rate than elsewhere in the aluminium matrix. As previously mentioned, the oxide formed on top the intermetallics will have a more porous structure than the oxide formed on the adjacent Al matrix. When the metal is immersed in an aqueous solution, the oxide will transform into a bilayer structure, which consists of a less compact barrier layer (highly defective) and a highly porous outer layer. In this case, the aqueous solution is likely to directly interact with the barrier layer and most likely with the intermetallic itself. Consequently, the continuous transport of water molecules and anions through the defective
double layer will inhibit the passivation of the region promoting selective dissolution of the intermetallic (selective dealloyment). Another and equally important influence of intermetallics on the Al matrix is strictly related to their depolarization effect (a.k.a. galvanic coupling). The different composition of the solute-depleted Al matrix and the solute-rich intermetallics produces galvanic cells leading to the dissolution of the less noble areas (see Figure 5). This aspect has been well studied in several papers for different aluminium alloys [54, 55, 56, 57, 58]. Additionally under polarization conditions, the pitting potential of intermetallics is found to vary according to their composition and, most of the time, differing to the pitting potential of the aluminium matrix [56, 59]. That is, depending on the intermetallic’s chemical composition, its pitting potential can be more positive or more negative compared to the pitting potential of the bulk metal.

3.7 Summary

Alloying elements can contribute to the formation of the oxide layer modifying its final composition and the way this oxide layer interacts with the aqueous media. Base on Macdonald and Habazaki et al. theory, it is possible to elucidate which alloying elements are most favoured to incorporate into the oxide layer. Magnesium is found to be the most favoured alloying element to contribute to the formation of the oxide layer in aluminium alloys. However, the extend of the enrichment will strongly depend on other factors such as charge of the species, activation energy of the alloying additions, bulk concentration of these alloying additions, temperature and mobility of the alloying additions in the aluminium oxide layer. In addition, intermetallics induce the formation of defects (weak spots) as well as composition changes in the oxide layer, eventually making it difficult the growth of protective layer. These weak spots caused by intermetallics can originate localized corrosion. However, a proper understanding of the localized corrosion process (in particular the intergranular corrosion process) should include a proper study of the initiation of localized corrosion attack beyond the sole formation and composition of intermetallics.
3.8 References

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Chapter 4

Composition of the Oxide Layer Formed on 5XXX Aluminium Alloys and its Electrochemical Behaviour in Aqueous Solution

4.1 Introduction

In the aluminium industry, aluminium alloys containing small concentrations of Mg are a class of materials that have great commercial interest because their improved mechanical properties compared to pure aluminium [1,2]. However, segregation of Mg in Al-Mg alloys when exposed to thermal treatments during fabrication or service conditions brings undesirable changes to the surface and bulk metal [3]. Mg surface enrichment can stimulate environmental sensitivity of the alloy, which also encourages localized reactivity and hydrogen entry [4]. Additionally, compared to Mg-free aluminium alloys, more alloy pick-up occurs during machining, welding becomes a problem [5], adhesion and aging of applied organic coatings such as paints and adhesives are frequently poor because of the susceptibility to hydrolysis of magnesium oxide [6]. Also, unacceptable surface stains arise during certain heat treatments due to excessive Mg enrichment. Hence, the benefits to bulk properties of aluminium attained by using Mg as a solid solution strengthener are traded for disadvantages arising directly from the surface activity of magnesium.

Although there is no extensive literature on surface segregation on 5XXX aluminium alloys, there are several studies that have shed some light in the understanding of the magnesium enrichment mechanism. Earlier, most of the understanding of Mg oxide enrichment was accumulated from phenomenological observations during heat treatments of Al-Mg alloys [7]. The advent of improved surface analytical techniques (e.g. Auger, XPS, XRD, SIMS, etc.)
have made possible to determine the chemical composition of oxide films and estimate their
thickness with high resolution and accuracy. Numerous theoretical studies have also been
published that add information to the segregation mechanism, especially at high temperatures
[8, 9, 10, 11]. Despite these positive advances, there is still an unclear picture about the
structure of the oxide layer as well as the mechanisms of Mg segregation to the metal surface.
Consequently, there are some discrepancies on the results reported in literature about the
degree of enrichment on this type of alloys. For instance, Lea and Molinari [12] measured the
surface composition of Al-Mg alloys with 0.8wt% and 2.5wt% Mg using Auger electron
spectroscopy (AES) in the temperature range up to 600°C. They found that the surface
enrichment ratio (Mg\textsubscript{surf} / Mg\textsubscript{bulk}) was about 24 at 100°C, falling to about 12 at 200°C. At
temperatures above 200°C, the magnesium evaporation exceeded the segregation. As a result,
they established that surface enrichment at temperatures above 250°C is in practice not
observed [12]. Similarly, Esposto et al. [13] measured the Mg surface segregation of a (110)
Al-Mg (1.2wt% Mg) single crystal alloy at 500K (227°C) and obtained an enrichment of
approximately 42wt% Mg. They also found that evaporation of Mg at the alloy surface began
slightly above 500K. In contrast, Saied and Sullivan [14] observed also by means of AES an
increase in Mg segregation and an increase in enriched layer depth with temperature in Al-
1.0at% Mg alloy at temperatures above 500K. They reported an enrichment of 5wt% at 623K
(350°C) in the alloy. A similar result was reported by Wefer [15]. Holub et al. [16] reported
an enrichment of 67% MgO on the surface of a commercial AA5052 alloy with 2.64wt% Mg
sensitized at 370°C for 1 hour. In addition, they found a dependency of the magnesium
enrichment as a function of temperature and Mg content in the alloy. However, they reported
that Mg segregation occurs only at temperatures above 250°C [16].

The structure of the oxide layer in Al-Mg alloys is also the source of additional debate. For
instance, Wakefield et al. [17] studied the oxide composition of high Mg content Al-Mg
alloys (9.5wt% and 11wt%) at room temperature, 200°C and 300°C. They reported that at
20°C, the oxide consisted predominantly of aluminium oxide (70%) with a minor contribution
of magnesium oxide (30%). At 200°C and 300°C, the oxide is predominantly magnesium
oxide while at 430°C it is entirely MgO. Shimizu et al. [18] reported the existence of a
MgAl\textsubscript{2}O\textsubscript{4} spinel dividing the Al\textsubscript{2}O\textsubscript{3} and MgO layers. Scotto-Sheriff et al. [19] suggested a
structure for the oxide layer (depicted in Figure 4-1) comprising of a MgO inner layer and an
Al₂O₃ outer layer (Figure 1a). If the alloy is exposed to annealing temperatures, the oxide structure will transform in a predominantly MgO layer with small patches of Al₂O₃ (Figure 4-1b).

![Diagram of oxide layer structure](image)

**Figure 4-1. Oxide layer structure model and distribution of elements according to Scotto-Sheriff et al. [19]**

Additionally, few researchers have studied the influence of Mg enrichment in the electrochemical behaviour of Al-Mg alloys [19, 20, 21]. For example, Baer *et al.* [21] found that because of the high reactivity of Mg, the magnesium surface enrichment may have little or no effect on the hydration of the surface and, consequently, no effect in the electrochemical open circuit potential (OCP) of the metal. On the other hand, Scotto-Sheriff and co-workers also found that the thickness of the layer, the amount of magnesium oxide, and its dissolving resistance in water are strongly modified by the annealing process [19]. For this reason, the aim of the present chapter is to explore the role of magnesium enrichment in the electrochemical behaviour of Al-Mg alloys, and its effect on the composition of oxide layer as a function of moderate sensitization temperatures.

### 4.2 Experimental

All samples were cut from three commercial wrought aluminium alloy sheets in tandem rolled conditions (hot rolled until obtaining a final thickness of 8mm for AA5018, 4.5mm for AA5754 and 3.5mm for AA5083). The chemical composition of each alloy was obtained by spark emission spectrometry and the results are displayed in Table 4.1. The samples were
ground with a 600-grit SiC (silicon carbide) grinding paper removing approximately 1.5mm from the surface. This particular sample preparation process permitted the elimination of the existing deformed oxide layer produced by the fabrication process [22, 23], obtaining in this way a more representative aluminium oxide on all samples with no MgO enrichment before experimentation. Prior to the heat treatment, the samples were degreased and cleaned in ethanol using an ultrasonic bath for 5 minutes. Finally, the metal samples were sensitized in an air-circulating furnace at temperatures of 100°C and 200°C, each one for periods of 5, 11 and 30 days followed by air-cooling until room temperature was achieved.

Table 4.1. Elemental composition of Al-Mg alloys (wt%), obtained by spark emission spectrometry.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
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<td>AA5754</td>
<td>2.74</td>
<td>0.77</td>
<td>0.11</td>
<td>0.30</td>
<td>0.01</td>
<td>0.06</td>
<td>0.06</td>
<td>0.01</td>
</tr>
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<td>AA5018</td>
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<td>0.52</td>
<td>0.14</td>
<td>0.32</td>
<td>0.02</td>
<td>0.13</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>AA5083</td>
<td>4.52</td>
<td>0.62</td>
<td>0.15</td>
<td>0.36</td>
<td>0.02</td>
<td>0.09</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The surface composition and depth profiles were obtained by Auger Electron Spectroscopy (AES). These experiments were done in the department of metallurgy, electrochemistry and materials science of the Vrije Universiteit Brussels. All measurements were performed on a PHI 650 scanning Auger microprobe (SAM) system with a relative energy resolution \( \Delta E/E \) of 0.25%. The primary electron energy and beam current were set at 5 KeV and 20 \( \mu \)A, respectively. The electron beam was set to scan an area of approximately 130 \( \mu \)m \( \times \) 130 \( \mu \)m. The ion sputtering was performed with an argon ions beam with a gun voltage of 3.5 kV and a gun current of 10 \( \mu \)A. The sputtered area was approximately 3 mm \( \times \) 3 mm. The system was calibrated to have an average sputtering rate of approximately 4nm/min (nanometer per minute) for \( \text{Al}_2\text{O}_3 \). Prior to each analysis, the surface of each sample was sputter-cleaned for 20 seconds. This surface pre-treatment permitted the elimination of possible surface contaminants that may influence the Auger spectra.

Auger electron spectroscopy (AES) enables analysis of a surface layer between 0.5 to 3 nm thick, depending upon the inelastic mean free path (IMFP) of the characteristic Auger electrons emitted. The IMFP can be defined as the distance an electron will travel before
undergoing an inelastic collision in which the electron loses part of its initial kinetic energy. Auger electrons with kinetic energies in the range of 25 to 3000 eV lose their characteristic energy within this thickness. When AES is used in conjunction with an argon ions sputtering which removes surface atom layers during the analysis, composition-depth profiles through the surface region can be constructed. It is necessary to keep in mind that both the peak intensities and the peak energies of the aluminium and magnesium Auger spectra are sensitive to their chemical environment (oxidation state) and, consequently, the peaks representing the metals are clearly differentiated from the peaks representing the oxides. Low energy Auger lines (L$_{2,3}$VV) for the metal and its corresponding oxide could be used for the surface analysis; however, these line are very sensitive to contamination [24]. For this reason, all interpretation of Auger spectra and composition-depth profiles done in this thesis were based on high energy KL$_{2}$L$_{2}$ Auger lines at 1396 eV for aluminium and 1378 eV for aluminium oxide. For magnesium and magnesium oxide, KL$_{2}$L$_{2}$ Auger lines occur at 1186 and 1174 eV, respectively. The element concentration was calculated taking in account the sensitivity factor for Al and Mg. These values are given in the Auger data handbook [59].

Finally, in order to correlate the changes of the oxide layer (Mg enrichment) and the electrochemical behavior of the surface, electrochemical open circuit potential (OCP) measurements were performed for a period of 24 hours. The experiments were carried out using a 0.6M (mole/liter) sodium chloride (NaCl) pH=3 electrolyte solution, limiting the exposed sample area to 1 cm$^2$. The solution pH was adjusted by the addition of hydrochloric acid (HCl). The data was acquired by employing a Solartron SI-1286 electrochemical unit.

Additionally, pH monitoring for each sensitized sample as a function of time was performed with a Schotto-CG842 pH-meter that has a pH resolution of $\pm 0.01$ in the temperature range of 15°C to 35°C. The main objective of the pH monitoring was to measure the surface pH changes near the metal surface as a function of time and as a function of Mg enrichment. In order to increase the sensitivity of the probe and to acquire a surface reading near the metal surface, a Teflon Luggin probe was adapted to the pH electrode. The tip diameter of the Luggin probe was 2 mm and placed at approximately 4 mm above the metal surface. The total exposed area of the metal surface to the electrolyte was fixed to 1 cm$^2$. A diagram of the experimental set-up is shown in Figure 4-2. Prior to each measurement, the pH meter was
calibrated with commercial buffer solutions pH= 2, 4 and 7. Each pH monitoring experiment was carried out in a 0.6M NaCl pH 3 solution for a period of 24 hours.

![Experimental set-up used for pH monitoring of the metal surface as a function of time and as a function of Mg enrichments.](image)

Figure 4-2. Experimental set-up used for pH monitoring of the metal surface as a function of time and as a function of Mg enrichments. The solution used was 0.6M NaCl pH 3 at room temperature.

### 4.3 Results

#### 4.3.1 Surface enrichment

Figure 4-3 shows the surface Auger spectra of AA5754, AA5018 and AA5083 alloys with natural formed oxides. It is evident from Figure 4-3, the oxide layer formed at room temperature is a mixture of aluminium oxide (Al₂O₃) and magnesium oxide (MgO), and the concentration of MgO seems to be influenced by the Mg content in the bulk metal. These results are different to those found by Goldstein and Dresner [25], and Shamir et al. [26]. They stated that the natural oxide consisted solely of aluminium oxide, which was determined to be amorphous Al₂O₃. Even though the oxide layer is mainly composed of Al₂O₃, magnesium segregates to the surface and contributes in a minor way to the formation of the oxide layer as MgO.
Figure 4-3. Surface Auger spectra for different commercial Al-Mg alloys with different Mg bulk content in room temperature conditions.
Figure 4-4. Surface Auger spectra for different commercial Al-Mg alloys with different Mg bulk content treated at 200°C for 11 days
Treatment of the Al-Mg samples at intermediate temperatures of 100°C and 200°C resulted in the formation of an oxide with a composition of the most outer surface layer enriched with MgO. Figure 4-4 displays the surface Auger spectra of the treated samples containing different Mg bulk concentrations at 200°C. Evidently, the degree of enrichment on the most outer part of the oxide layer appears to be influenced by the amount of magnesium in the bulk. Auger surface scans show how temperature induces changes in the outer part of the oxide layer.

Based on peak-to-peak ratios of the Auger surface scans, the relative amounts of Mg segregated to the surface as a function of sensitization temperatures for a fixed period of time (11 days) were calculated. The results of this calculation are shown in Figure 4-5. Evidently, the temperature applied to the alloyed metal influences the behavior of the Mg segregated to the surface. It is possible to observe that Mg surface segregation follows a parabolic (quadratic) rate process. This means that as the temperature is increased, a higher amount of Mg is segregated to the surface. Figure 4-5 also shows that the magnesium enrichment tends to be more pronounced in alloys with higher Mg content. In other words, high Mg enrichments will be obtained with high Mg content alloys at lower temperatures. On the other hand, low Mg enrichment will be reached with low Mg content alloys at higher temperatures. This behavior is consistent with the results reported by Holub et al. [16].

![Magnesium surface enrichment](image)

**Figure 4-5.** Mg surface enrichment as a function of temperature and Mg concentrations in the alloy.
4.3.2 Composition depth profiles
Auger composition-depth profiles (CDP) were made in order to determine the composition variation with depth through the oxide and estimate the thickness of the oxide layer grown at different temperatures. The profiles are expressed in atomic percentage (at%) and the symbols Al and Mg represent the concentration of the metal, whereas the $\text{Al}^{3+}$ and $\text{Mg}^{2+}$ represents the atomic concentration of aluminium and magnesium, respectively, in their oxide states. Composition-depth profiles are shown in Figures 4-7 and 4-8. As previously mentioned, the peak intensities and the peak energies of the aluminium and magnesium Auger spectra are sensitive to their chemical environment (oxidation state) and, consequently, the peaks representing the metals are clearly differentiated from the peaks representing the oxides. A typical shift of 7.5 eV between the aluminium metal peak ($\text{Al KLL}_{(m)}$) and the aluminium oxide peak ($\text{Al KLL}_{(ox)}$) located at 1386.5 eV enables an easy identification of the chemical state of aluminium (Figure 4-6a). In a similar way, a shift of 6 eV permits to identify the magnesium metal ($\text{Mg KLL}_{(m)}$) and magnesium oxide ($\text{Mg KLL}_{(ox)}$), typically located at 1180 eV (Figure 4-6b). This situation allows performing a separation of the metallic from the ionic Auger spectra as a function of depth.

![Figure 4-6](image_url)

Figure 4-6. Auger high energy peaks showing the difference between the metallic and oxide states of (a) aluminium and (b) magnesium.
Figure 4-7 show the CDPs of different Al-Mg aluminium alloys with different Mg bulk concentrations at room temperature conditions. The composition obtained for the natural formed oxide of each alloy indicates that Mg in the form of magnesium oxide contributes in a minor way to the formation of the oxide layer. Also, it is important to observe that the oxygen signal (O$^{2-}$) persists to great sputter depths, long after the strong metallic aluminium signal indicates that a large portion of the oxide layer has been removed. In all composition-depth profiles, aluminium metal coexists with Al$_2$O$_3$ and MgO over a large portion of the oxide thickness. This situation seems to be independent of the temperature. Figure 4-8 shows the CDPs of different Al-Mg alloys sensitized at 200°C for 11 days. In Figure 4-8, it is evident that the amount of Mg segregation through the oxide layer becomes dominant in the formation of oxide layer. By having a higher Mg content in the alloy, the degree of enrichment increases. If we compare the CDP of AA5754 and AA5083, it is possible to observe that the distribution of Mg through the oxide layer is not the same. For instance in AA5754 (Figure 4-8), the Mg$^{2+}$ signal shows fluctuations as sputtering depth increases, reaching a maximum concentration almost in the middle of the oxide layer. In contrast, for the alloy AA5083, the Mg$^{2+}$ signal appears to have a constant distribution approximately through half of the oxide layer’s thickness.

As previously stated, Al$_2$O$_3$ and MgO coexist over a large portion of the thickness ($Z_o$). However, the precise depth at which the oxide-metal interface exists cannot be clearly identified. For this reason, thickness of the oxide layer ($Z_o$) is defined as the mean depth sputtered at which the aluminium metal signal (Al) has risen to approximately 50% of its maximum value [27]. Comparing oxide thickness by this method should be taken as an estimation since the sputtering rate changes with composition. Differences in the sputtering yield between MgO and Al$_2$O$_3$ will be the most significant cause of variations in the sputtering rate. The sputtering yield for MgO is reported to be 0.7, whereas the sputtering yield for Al$_2$O$_3$ is 0.2 [28]; as a result, the sputtering yield for MgO is 3.5 times higher than for Al$_2$O$_3$ indicating that the etch rate for MgO is greater.
Figure 4-7. Concentration-depth profiles (CPD) for Al-Mg alloy at room temperature conditions.
Composition of the oxide layer formed on 5XXX aluminium alloys

**Figure 4-8.** Concentration-depth profiles (CPD) for Al-Mg alloys sensitized at 200°C.
4.3.3 Electrochemical behavior of the enriched surface

The electrochemical open circuit potential (OCP) of Al-Mg alloys with different Mg bulk contents were monitored for 24 hours in an acidified chloride containing solution (0.6M NaCl pH 3). The main objective of these experiments was to monitor the behaviour of the Mg enriched oxide layer in aqueous solution as a function of time.

The electrochemical open circuit potential vs. time can be described as the study of the time behaviour of the electrode potential in the absence of current flowing through the electrode. Despite the absence of net current, the electrode interface undergoes a dynamic transformation reflected as time dependent potential variations. When these potential variations are independent of time, then it said that the open circuit potential has reached steady state.

In every real metal surface there are anodic and cathodic areas that contribute to the corrosion process. Hence, a necessary and sufficient condition for corrosion is that the anodic reaction (metal dissolution) and the cathodic reaction proceed simultaneously at the metal/aqueous solution interface. The anodic and cathodic reaction can be represented as two partial current densities: a cathodic partial current density \( i_c \) and an anodic partial current density \( i_a \). These current densities can be expressed as

\[
\text{(cathodic partial current density)} \quad i_c = nFk_\text{Exp} \left( -\frac{\beta VF}{RT} \right) C_{sol} \quad (A)
\]

\[
\text{(anodic partial current density)} \quad i_a = nFk_\text{Exp} \left( 1 - \beta \right) \frac{VF}{RT} C_{sol} \quad (B)
\]

where \( n \) is the number of moles of electrons required to complete one act of the reaction, \( \beta \) is a symmetry factor, \( F \) is the Faraday constant, \( k_\text{r+} \) represent the chemical rate constant (anodic or cathodic), \( C_{sol} \) is the solution concentration, \( VF \) is the energy associated to the passage of charge through the potential difference of the double layer.
The time-varying interface is affected by several factors such as type of solution, concentration, pH, and temperature of the solution. In addition, the characteristics of the surface also play an important role such as surface composition, hydration properties, and surface charge characteristics. For this reason, the transients provide additional information on the metal’s behavior in aqueous solution. The time dependence of the open circuit potential can be described as

\[
\frac{d(V)}{dt} = -\frac{i_o}{C_{DL}} \left[ e^{(1-\beta)VF/RT} - e^{-\beta VF/RT} \right],
\]

where \( V \) is the changing potential difference across the bi-layer as a function of time, \( i_o \) is the exchange current density (this parameter reflects the kinetic properties of the particular interfacial system and can vary from one reaction to another, and from one electrode material to another [27]), and \( C_{DL} \) is the capacitance of the double layer reflecting its ability to store charge. In this equation, it can be observed that changes in the OCP with time are related to the effects of the anodic and cathodic reactions. These reactions contribute to the formation of a protective layer on the surface of the metal. Thus, the anodic and cathodic reaction can also be referred as the rate of formation and the rate of dissolution reaction of the protective film.

Figure 4-9 compiles the OCP behavior of for AA5754 (2.7% Mg) treated and untreated, and the OCP behavior of aluminium (99.5%). The OCP behavior of aluminium (immersed in an acidified NaCl solution) is described by a drop on the OCP from -0.735\( V_{SCE} \) to a value of about -0.873\( V_{SCE} \), within the first 4 hours of immersion. Immediately after, the potential steadily decreases to more active potentials at a rate of 2.11 mV/hour. In the case of an untreated Al-Mg alloy (2.7%Mg), the OCP shows some differences from the behavior observed for aluminium. During the first 1.5 hours, the alloy’s behavior is characterized by a sharp drop on the potential from -0.755\( V_{SCE} \) to a value of approximately -0.954\( V_{SCE} \), followed by small potential increment of 10 mV. After this potential increment, the OCP slowly decreases until achieving a steady potential of -0.956\( V_{SCE} \) independent of time. As the sensitization temperature increases, the transient behavior of the alloy becomes more evident. At 100\(^{\circ}\)C, it is observed that the open circuit potential suffering a marked drop from -0.766 to -0.981\( V_{SCE} \) within the first 2 hours of immersion. Subsequently, the potential experiences a
small rise of about 10 mV to later decline again to approximately $-1.00\text{V}_{\text{SCE}}$. Finally, the potential steadily increases at a rate of 6.17 mV/hour tending to a value of $-0.956\text{V}_{\text{SCE}}$. At a temperature of 200°C, the alloy shows its characteristic sharp drop from -0.922 to $-1.064\text{V}_{\text{SCE}}$ within the first hour of immersion. In this particular case, the OCP starts to rise and, after 13 hours, achieves a steady rate of increment of 2.64 mV/hour. After 22 hours of immersion reaches a steady state potential of $-0.956\text{V}_{\text{SCE}}$. The relationship between the strongest fluctuation in the transient (more negative potentials) and the sensitization temperature seems to correlate with the amount of Mg enrichment shown in the composition profiles. When the behaviour of AA5754 alloy is compared to aluminium (99.5%Al), it can be observed that the OCP of aluminium does not show strong variations. Additionally, the OCP of aluminium decreases slowly as time elapses suggesting that, for a period of time long enough, the OCP eventually will reach the same potential as for AA5754 alloy.

![Figure 4-9. Electrochemical open circuit potential curves of AA5754 (in non-sensitized and sensitized conditions) and AA1050 immersed in 0.6M NaCl pH 3 electrolyte solution.](image)

For higher Mg content alloys (4.5wt% Mg), the OCP shows a more distinctive behaviour as it can be seen in Figure 4-10. For the non-sensitized alloy, it is possible to observe the characteristic marked potential drop from -0.770 to $-0.999\text{V}_{\text{SCE}}$ within the first hour of immersion. Immediately after, the OCP increases to a maximum value of $-0.841\text{V}_{\text{SCE}}$. 
Afterwards, the potential slowly declines at a steady rate of 1.95 mV/hour. At 100°C, the potential shows again a sudden potential drop from -0.800 to -1.19V_SCE. Similarly as for the non-sensitized alloy, the potential rises to a maximum value of -0.926V_SCE to later slowly decrease at a rate of 3.96 mV/hour. However, after 18 hours of immersion, the OCP achieves a steady state potential (independent of time) of -0.956V_SCE. At 200°C, the OCP behaviour loses its characteristic rapid potential drop. This time the potential experiences a rather pronounced increment from -1.066 to -0.978V_SCE, and subsequently steadily increases at a rate of 2.80 mV/hour. After 20 hours of immersion, the OCP achieves a steady state value of -0.956V_SCE.

The sharp initial drop on the OCP could be associated to magnesium enrichment on the surface as indicated in the Auger composition profiles. In fact, the potential increment during the first few hours can be related to the dissolution of MgO, the subsequent formation of the aluminium oxide/hydroxide layer trying to achieve a steady state rate of formation and rate of dissolution of the film. Interestingly, the OCP of the alloys with 4.5%Mg and the OCP of aluminium seem to converge to a potential value of approximately -0.956 V_SCE indicating that Mg enrichment eventually disappears allowing the aluminium oxide/hydroxide to control the electrochemical behaviour of the alloy. This effect could be achieved if the monitoring time for the OCP is extended beyond 24 hours.

Figure 4-10. Electrochemical open circuit potential curves of AA5083 (in non-sensitized and sensitized conditions) and AA1050 immersed in 0.6M NaCl pH 3 electrolyte solution.
The dissolution reaction of Mg(OH)$_2$ and Al(OH)$_3$ can contribute to pH changes near the metal surface by releasing OH$^-$ ions that decrease the H$^+$ ion concentration near the surface of the metal. Magnesium hydroxide is only slightly basic, whereas aluminium hydroxide exhibits either acidic or basic properties (amphotericism) depending on the reaction in which it is involved. In our experimental conditions, Al(OH)$_3$ reacts as a base in our acidified NaCl solution. A similar reaction can be observed in the presence of common acids such as with sulphuric acid (H$_2$SO$_4$) forming aluminium sulphate (Al$_2$(SO$_4$_3)). In contrast, Al(OH)$_3$ is found to react as an acid in the presence of strong bases to form aluminates; for example, with sodium hydroxide (NaOH) to form sodium aluminates (Na[Al(OH)$_4$(OH)$_2$$_2$]).

Due to its specific chemical characteristics, magnesium-rich surfaces induce a more severe change on the solution’s pH affecting the overall electrochemical behaviour of the metal. This situation is well observed in magnesium alloys which oxide layer consists entirely of MgO. Figure 4-11 displays the effects that this Mg-rich oxide has on the pH near the metal surface of an Mg alloy when immersed in an acidified (pH=3) NaCl solution and compared to the effect of dominant aluminium oxide layer.

![pH changes as a function of time](image)

Figure 4-11. pH surface changes as a function of time induced by the presence of a Mg-rich oxide layer in 0.6M NaCl pH 3 electrolyte.
It is evident from Figure 4-11 that the hydration of the Mg oxide layer, its subsequent reaction to form a hydroxide and its final incorporation to the electrolyte induce an alkalization near the metal surface. This alkalization occurs rapidly during the first 2 hours of immersion to later slow down until reaching a limiting pH value of 10 after 40 hours of immersion. In contrast, the changes induced on the pH by the hydration of the aluminium oxide layer are much less drastic.

The incorporation of Mg to the aluminium oxide layer induces changes similar to the changes described above. Figure 4-12 shows the pH surface changes due to a Mg-enriched oxide layer in Al-Mg alloys. The dissolution of Mg(OH)$_2$ shows to have a more noticeable effect on the pH than Al(OH)$_3$. It is possible to see from Figure 4-12 that alkalization due to Mg dissolution is fast during the first 3 hours of immersion. After this period, the pH seems to reach a limiting value. This value is dependent of the amount of Mg present in the oxide layer. The higher is the amount of Mg present in the oxide layer, the stronger the pH changes near the metals surface and vice versa. Later on this chapter, we will try to correlate the pH behaviour as shown in Figure 4-12 with the transient behaviour observed on the open circuit potentials shown in Figures 4-9 and 4-10.

![pH changes as function of time](image)

Figure 4-12. pH surface changes as a function of time for Al-Mg alloys sensitized at 200°C. Solution used is 0.6M NaCl pH 3.
Mg surface enrichment is observed to increase with temperature and Mg bulk content. However, at room temperature and after the removal of the previous oxide layer, a small Mg concentration segregated to the newly natural formed oxide can still be measured as seen in the CDPs in Figure 4-7. It is well known that there are different oxide growth mechanisms at high and low temperature. It is generally accepted that field controlled diffusion predominates at low temperatures. As temperature increases, thermally activated diffusion is obtained changing the rate from a parabolic oxidation rate to a linear relationship \((T >350^\circ \text{C})\). At room temperature, the oxide consists predominantly of \(\text{Al}_2\text{O}_3\) and a small contribution of MgO content which is higher than the magnesium bulk content. In contrast at 200\(^\circ\)C, the oxide is mainly comprised of MgO. However, it is believed that MgO is not distributed uniformly along the metal surface. In other words, the amount of surface enrichment will depend on several factors such as grain orientation, number of precipitates present on the surface, roughness of the metal surface and type of oxide layer (crystalline vs. amorphous).

At low temperatures, migration of solute atoms is driven by a high electric field gradient and the rate-determining step in the oxidation process may then be the diffusion of ions from the metal-to-metal vacancies. As also mentioned in Chapter 3, the oxide formed at room temperature is mainly a metal-deficient oxide. That is, aluminium metal vacancies may be the predominant defects existing in the oxide layer. These metal vacancies are formed through the reaction of oxygen with the oxide layer. Consequently, the diffusion process by the influence of an electric field preferentially favors the transport of the trivalent aluminium ions and, secondly, the transport of the divalent magnesium.

At 100\(^\circ\)C and 200\(^\circ\)C, Mg segregates to the oxide layer mainly through thermally induced diffusion. The higher oxygen affinity that Mg possesses compared to the oxygen affinity of aluminium (the heat of oxide formation is 371.2 kJ/mol for \(\text{Al}^{3+}\) and 1202.2 kJ/mol for \(\text{Mg}^{2+}\)), helps to increase the migration of Mg to the metal surface [30, 31]. Moreover, \(\text{Mg}^{2+}\) ions have greater outward relative mobility than \(\text{Al}^{3+}\) ions, which is reported to be consistent with the magnitude of the single metal-oxygen bond energies, namely 166 kJ/mol for Mg-O and 280 kJ/mol for Al-O [32]. Shimizu and Kobayashi have shown that the relative migration rates of foreign cations in anodic alumina can be correlated to energies of their single metal-oxygen bond, suggesting the importance of bond breaking in the ionic transport process [33].
Since the Mg-O bond can be easily broken, the mobility of Mg ions (Mg\(^{2+}\)) through the oxide layer is less inhibited. The Al-O bond is a stronger bond that limits the mobility of Al ions that can travel through the oxide, and consequently, most of them remain in the area near the metal/oxide interface whereas Mg ions tend to occupy the outer part of the oxide layer (oxide/air interface).

### 4.3.4 Time dependence of Mg segregation

If bulk diffusion is the rate limiting mechanism in surface segregation, then it is possible to describe the segregation of Mg to the free surface as a function of time by using an equation introduced by Lea and Seah [34]. In the absence of evaporation, the time dependence of the Mg surface concentration is given by

\[ C_s = \alpha \cdot C_\infty \left[1 - \exp(x^2)erfc(x)\right], \quad (1) \]

where \( x = \sqrt{Dt/\alpha^2 d^2} \), D is the diffusion coefficient, t is the time, \( C_s \) is the surface concentration of magnesium at time t, \( C_\infty \) is the solute concentration at t = \( \infty \) and \( \alpha \) is the enrichment factor given by the ratio between the Mg surface concentration and the Mg bulk concentration.

Figure 4-13 displays the result obtained by fitting the experimental values with Eq. (1). Right away, it is evident that this equation does not give a satisfactory fit of the data. Attempts to force a fit have yielded parameters with values that are much smaller compared to those values shown in Table 4.2.

<table>
<thead>
<tr>
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<th>( D_0 ) (m(^2)/sec)</th>
<th>Q (KJ/mol)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al in Al</td>
<td>22.5x10(^{-4})</td>
<td>145</td>
<td>[35]</td>
</tr>
<tr>
<td>Al in Al</td>
<td>19.8x10(^{-4})</td>
<td>143</td>
<td>[36]</td>
</tr>
<tr>
<td>Mg in Al</td>
<td>1.49x10(^{-5})</td>
<td>120</td>
<td>[37]</td>
</tr>
<tr>
<td>Mg in Al</td>
<td>2.00x10(^{-6})</td>
<td>117</td>
<td>[12]</td>
</tr>
<tr>
<td>Mg in Al</td>
<td>0.60x10(^{-6})</td>
<td>125</td>
<td>[38]</td>
</tr>
<tr>
<td>Mg in Al(_2)O(_3)</td>
<td>4.62x10(^{-2})</td>
<td>75</td>
<td>[41]</td>
</tr>
<tr>
<td>Mg in MgO</td>
<td>74.6x10(^{-4})</td>
<td>384</td>
<td>[39]</td>
</tr>
<tr>
<td>Mg in MgO</td>
<td>4.4x10(^{-8})</td>
<td>234</td>
<td>[12]</td>
</tr>
</tbody>
</table>
Figure 4-13. Normalized Mg concentration ratio of AA5018 as a function of sensitizing time at 100°C. Dots indicate experimental values of AA5018 sensitized at 100°C whereas the smooth curve indicates fitted values using Eq (1).

For this reason, a modified version of Bloch’s [40] empirical relation is employed which is based on a nucleation and growth kinetics law

$$x_s = x_o + x_m[1 - \exp(-\kappa t)], \quad (2)$$

where $x_s$ is the surface concentration, $x_o$ is the initial enrichment found in the oxide, $x_m$ is the mean solute concentration found in the oxide and $\kappa$ is a rate constant given by

$$\kappa = \kappa_o \exp(-Q/RT), \quad (3)$$

that can be related to the diffusion rate of ionic species. The parameter $x_o$ accounts for the initial enrichment measured in the Auger concentration profiles (Figure 4-6). In this case, Eq. (2) provides an excellent fit to the data as shown in Figure 4-14. In all cases, the segregation reaches a limiting Mg concentration on the surface indicating, at the same time, that the thickness of the oxide will eventually achieve a limiting value.
Composition of the oxide layer formed on 5XXX aluminium alloys

Figure 4-14. Mg surface concentration in Al-Mg alloys as a function of time and temperature. Data fitted with Eq. (2)
The activation energies for segregation found for Mg\(^{2+}\) in Al\(_2\)O\(_3\) by using Eq. (2) and (3) are: \(Q_1 = 9.51\) kJ/mol for AA5754, \(Q_2 = 17.89\) kJ/mol for AA5018 and \(Q_3 = 21.02\) kJ/mol for AA5083 which are lower than the values found in published literature. Nevertheless, these activation energies reflect the ease at which Mg\(^{2+}\) moves in the Al\(_2\)O\(_3\). Lea and Ball [41] showed that the activation energies for Mg\(^{2+}\) in Al\(_2\)O\(_3\) are about 75 kJ/mol for oxides in dry air and 37 kJ/mol for moist oxides. In addition, Linder et al. [42] found that the activation energy for Mg\(^{2+}\) in MgO is 330kJ/mol. Therefore, this situation indicates that once the MgO area in the oxide layer continues to grow, the mobility of Mg\(^{2+}\) is greatly damped preventing them from building a thicker MgO layer. Thus, the oxide layer on the Al-Mg alloy will reach a limiting thickness. Consequently for the layer to grow, it is necessary to supply more energy to the Mg\(^{2+}\). This situation can be easily achieved by increasing the temperature of the metal.

### 4.4 Discussion

#### 4.4.1 Behaviour of the enriched oxide layer in aqueous solution

The interaction between the Mg-rich oxide layer and an aqueous solution is particularly different from other aluminium alloys. Due to the surface enrichment, the electrochemistry of the surface interface is dominated by the magnesium oxide. Mg dissolves in most aqueous solutions in the pH range of 0 to 12.0, and only at a pH range of 12.5 to 15 Mg is capable of forming a passive protective magnesium hydroxide ((Mg(OH)\(_2\)) layer. Under particular experimental conditions, Mg is expected to immediately dissolve away from the passive film after immersion in non-alkaline solution. However, OCP measurements in 0.6M NaCl (Figure 4-9 and 4-10) show that this dissolution does not occur instantly. Instead, the existing oxide layer undergoes a chemical and structural transformation that seems to take place within the initial five hours of immersion in the aqueous solution.

This transformation comprises hydration of the surface and a subsequent change of the oxide film into a mixed-composition bilayer structure as described in Chapter 3. Due to its higher oxygen affinity, Mg will tend to react faster than aluminium to non-metals (e.g. H\(_2\)O, chloride, oxygen, fluorine, etc.). Consequently, Mg will react preferentially to humidity or
Compositon of the oxide layer formed on 5XXX aluminium alloys

highly wet environments [43]. The Mg-rich oxide layer will interact first with the aqueous solution transforming into a (porous) magnesium hydroxide layer. The stability of Mg(OH)$_2$ as a solid phase is only achieved under strong alkaline conditions. Under non-alkaline conditions, Mg(OH)$_2$ will dissociate and incorporate into the electrolyte as Mg$^{2+}$ and OH$^-$. When magnesium hydroxide is totally dissolved, it leaves a layer of Al(OH)$_3$ or AlO(OH) on the metal surface. This process is depicted in Figure 4-15. The sharp drop observed on the OCP curves during the first hours of immersion can be associated with the dissolution of the Mg-rich layer. The potential increments can be related to the subsequent formation of an aluminium oxide/hydroxide layer and the subsequent achievement of a steady rate of formation and dissolution of the film after 8 hours of immersion.

![Diagram showing the dissolution of the enriched oxide layer in Al-Mg alloys](image)

**Figure 4-15. Surface dissolution of the enriched oxide layer in Al-Mg alloys**

Due to the dissolution of Mg(OH)$_2$ porous layer, the pH near the surface increases as a direct result of the Mg(OH)$_2$ dissociation and incorporation to the electrolyte as seen in Figure 4-12. Hence, the alkalinity of the solution comes from the dissolution of Mg(OH)$_2$ rather than from the dissolution of Al(OH)$_3$. Strong pH changes were observed by Nordlien et al. [43] in pure Mg metals when immersed in distilled water. They have reported that after 48 hours of immersion, the pH of water increased to about 11. The results suggest that the rates of dissolution of the Mg-rich oxide layer as well as the changes of the surface pH can be correlated to the degree of Mg enrichment on the surface. When the changes in pH as a function of time are directly compared with their open circuit potentials, it can be observed
that the transients on the OCP are induced by the dissolution of the most reactive species (i.e. Mg(OH)$_2$) as shown in Figure 4-16. Immediately after the dissolution of the magnesium hydroxide species, the aluminium hydroxide (Al(OH)$_3$) layer takes control of the surface reaction of the metal. Since the pH of the solution used (pH 3) is outside the stability region of Al(OH)$_3$, dissolution of this hydroxide phase proceeds but at a slower rate. This situation is observable after 8 hours of immersion as a linear variation between the open circuit potential and the pH (Figure 4-16). The linear variation of the OCP and the pH are a direct manifestation of the equilibrium charge state between the surface and the solution.

An equilibrium distribution of charges of a semiconductor in an electrolyte solution (in the absence of applied polarization) is usually obtained by the knowledge of the flat-band potential ($V_{FB}$). A so-called Nernstian variation of $V_{FB}$, defined as a linear variation between $V_{FB}$ and the pH, indicates that the equilibrium of surface charges is controlled by the acid-base exchange of the surface sites with H$^+$ and OH$^-$ solution ions [44, 45]. This Nernstian variation of the $V_{FB}$ is normally accompanied by a parallel variation of the OCP, as it is observed in this case.

### 4.4.2 Acid-base characteristics of the magnesium-rich oxide layer

As mentioned earlier in Chapter 3, the acid-base properties of the oxide layer play an important role in the interfacial reactions. The most significant entities affecting the specific adsorption of the oxide layer are the adsorption of H$^+$ and OH$^-$ due to the acid-base reaction. Also in Chapter 3, we introduced an important parameter controlling the surface charge and the adsorption properties of the oxide layer called the pH of zero charge ($\text{pH}_{PZC}$). The $\text{pH}_{PZC}$ depends strongly on the characteristics of the oxide layer such as the surface stoichiometry, the degree of hydration, the semiconducting properties of the oxide, the crystallographic structure, the ratio of bonds exposed to the solution, the difference in the acidic and basic dissociation constants of surface hydroxyl groups, and impurities.
Composition of the oxide layer formed on 5XXX aluminium alloys

Figure 4-16. Open circuit potential (E) and surface pH variations as a function of time for different Al-Mg alloys
The \( \text{pH}_{\text{PZC}} \) parameter has been used in the characterization of aluminium oxide surfaces modified by ion-implantation. Natishan et al. [46] found that the \( \text{pH}_{\text{PZC}} \) of the modified oxide can be correlated to their pitting potential (\( E_{\text{pit}} \)). Bockris et al. [47] showed that this correlation is linear. In addition, McCafferty [48] found a linear relationship between \( E_{\text{pit}} \) and the flat-band potential (\( V_{\text{FB}} \)) of the surface, given by

\[
E_{\text{pit}} = 0.801 + 1.69V_{\text{FB}}
\]  

and this linear relation can be related to the \( \text{pH}_{\text{PZC}} \) as

\[
V_{\text{FB}} = -0.1400\text{pH}_{\text{PZC}} + \text{Const.}
\]

this approach was adopted and applied to the magnesium-enriched oxide layer of Al-Mg alloys. Hence, the enriched surface layer can be characterized by its acid-base properties using the \( \text{pH}_{\text{PZC}} \), and correlate this parameter to its corrosion properties such as its pitting potential. This approach takes in account two main assumptions: 1) the alloying element segregated to the metal surface is uniformly distributed in the oxide layer and no intermetallics are formed, and 2) the oxide does not show a different chemistry on its surface as compared to the interior of the layer. Firstly, a couple of definitions and published correlations will be introduced.

In general, it is possible to correlate the electronegativity of the oxide layer (\( \chi(\text{oxide}) \)) with the \( \text{pH}_{\text{PZC}} \) of the oxide. Butler and Ginley [49] have shown that the electronegativity of the oxide is related to its surface charge characteristics as

\[
\chi(\text{oxide}) = 6.64 - 0.108\text{pH}_{\text{PZC}}(\text{oxide}),
\]

where the electronegativity of any oxide \( M_xO_y \) is defined as the geometric mean of the electronegativity of the oxide constituents.
Composition of the oxide layer formed on 5XXX aluminium alloys

\[
\chi(\text{oxide}) = [\chi(\text{Metal}) \chi(\text{Oxygen})]^{1/(e+1)}. \quad (7)
\]

The electron affinity of the oxide (EA(oxide)) is defined as

\[
EA(\text{oxide}) = \chi(\text{oxide}) - \frac{1}{2} E_g, \quad (8)
\]

where the \( E_g \) is the band gap of the oxide layer. McCafferty [48] found experimentally a linear relationship between the EA(oxide) and \( V_{FB} \) given by

\[
EA(\text{oxide}) = 4.85 + 0.776 V_{FB}. \quad (9)
\]

By combining equations (8) and (9), we obtain

\[
\chi(\text{oxide}) = 4.85 + 0.776 V_{FB} + \frac{1}{2} E_g; \quad (10)
\]

by inserting equation (10) in (6), we find a linear relation similar to equation (5)

\[
V_{FB} = -0.14 pH_{PZC}(\text{oxide}) + 0.664 E_g + 2.297, \quad (11)
\]

and by substituting (11) in equation (4), we obtain a relation that correlates \( E_{pit} \) and \( pH_{PZC}(\text{oxide}) \) given by

\[
E_{pit} = 4.683 - 0.236 pH_{PZC}(\text{oxide}) - 1.122 E_g. \quad (12)
\]

Equation (12) allows correlating the surface charge and the adsorption characteristics of the oxide layer through the \( pH_{PZC} \) parameter with the pitting potential. For instance in the case of \( \text{Al}_2\text{O}_3 \), the \( pH_{PZC}(\text{Al}_2\text{O}_3) \) is reported to be 9.1 [50]. Menezes [51] and Tuccio [52] reported an \( E_g \) for \( \text{Al}_2\text{O}_3 \) in the range of 2.8 to 4.5 eV. By taking a value of \( E_g=2.9 \) eV, we obtain \( E_{pit} = -0.7239 \) V. This value is in agreement with Natishan’s data [46] and our own results, where
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the \( E_{\text{pit}} \) obtained is -0.7057 V. The potentiodynamic polarization of AA1050 (99.5% Al) in 0.6M NaCl pH 3 solution is displayed in Figure 4-17.

In the case of the Mg-rich oxide layer, we first need to calculate \( pH_{PZC} \) of the mixed alloy. This parameter can be estimated by using an ideal mixing law expressed as follows:

\[
\text{\( pH_{PZC} (Alloy) = f_{MgO} \cdot pH_{PZC} (MgO) + (1 - f_{MgO}) \cdot pH_{PZC} (Al_2O_3). \)}
\]

where \( f_{MgO} \) is the mole fraction of the Mg surface enrichment; If \( f_{MgO} = 0 \) which corresponds to an \( Al_2O_3 \) layer, then \( pH_{PZC}(Alloy) = pH_{PZC}(Al_2O_3) \). On the other hand, if \( f_{MgO} = 1 \) which indicates an entirely MgO layer, then \( pH_{PZC}(Alloy) = pH_{PZC}(MgO) \). Parks [53] and Butler et al. [49] measured the \( pH_{PZC} \) for MgO and obtained a value of 12.4. The \( E_g \) for MgO is estimated to be 7.7eV [49]. However for an oxide with mixed composition, \( E_g \) may be considered to be constant and equal to the \( E_g \) of the host oxide. This assumption is based on results found in literature; for example, Kamkin et al. [54] found that, in a series of Ti-Al alloys (10-50at% Al), the band gap of the oxide layer was essentially independent of alloy composition. Kim et al. [55] also found that, in ZnO films doped with Al, there was a small change in the \( E_g \) values. They obtained \( E_g = 3.3eV \) for pure ZnO, 3.52eV for 1wt% \( Al_2O_3 \), 3.54eV for 3wt%\( Al_2O_3 \), and 3.47eV for 5wt%\( Al_2O_3 \). Therefore, as a first estimation, it is possible to assume that for an enriched aluminium surface, \( E_g (Alloy) = E_g (Al_2O_3) = 2.9eV \).

Figure 4-17. Anodic polarization curves for AA5083 and Al in 0.6M NaCl pH 3 solution.
Composition of the oxide layer formed on 5XXX aluminium alloys

By applying Eq(12) to the Al₂O₃/MgO layer, we find that the estimation of the pitting potential for enriched surface oxides in Al-Mg can be divided in four cases:

- The oxide composition is almost or entirely dominated by the formation of MgO as in the case of sensitized high-Mg content Al-Mg alloys (e.g. AA5083). In this particular case, $E_g(MgO)= 7.7eV$ and $pH_{PZC}(alloy)=pH_{PZC}(MgO)=12.4$. Consequently the $E_{pit}$ for a MgO surface is estimated to be -0.689V. The experimental pitting potential obtained is $E_{pit} = -0.723V$.

- The oxide composition consists of 50%MgO and 50%Al₂O₃. Then, $E_g(alloy)=E_g(Al₂O₃)= 2.9eV$ and $pH_{PZC}(alloy)= 10.75$. Therefore, $E_{pit}$ is equal to -1.50V. This value does not agree with any experimental or published pitting potential.

- The oxide composition consists of 10%MgO and 90%Al₂O₃. In this case, the pitting potential found is $E_{pit} = -0.8019V$. The experimental value obtained was $E_{pit} = -0.723V$

- The oxide composition is almost or entirely dominated by Al₂O₃, Hence, we have $E_g(Al₂O₃)=2.9eV$ and $pH_{PZC}(alloy)=pH_{PZC}(Al₂O₃)=9.1eV$; thus, $E_{pit}=-0.72V$. The experimental value obtained for an aluminium metal (99.5% Al) is $E_{pit} = -0.706$, which is in good agreement with the predicted value.

It is interesting to see that the experimental pitting potentials obtained for Al-Mg alloys are similar to the pitting potential for aluminium. This behavior is explained by selective dissolution of Mg from the oxide. The selective dissolution of Mg from the oxide layer occurs as a result of the instability of MgO at the pH and chloride concentrations used in these experiments. Additionally, the selective dissolution of MgO shifts the pH of the remaining component, which is in this case Al₂O₃. Therefore, the surface charge characteristics of Al₂O₃ are more relevant than the characteristics for MgO.
It is known that the surface charge of the oxide layer is important in its interaction with a charged species, such as chlorides ions. Although the mechanism by which chloride ions penetrate the interior of the oxide layer is still debatable, it is possible to suggest a possible interaction process. The first step in the pitting process is the adsorption of \( \text{Cl}^- \) on the oxide-covered surface. When an ion interacts with an ionic surface such as an oxide, the attractive forces consist of [56]: 1) Coulombic forces, 2) electrostatic induction of the substrate by the approaching ion, 3) electrostatic polarization of the ion, and 4) non-polar van der Waals forces. Of these attractive forces, the largest effects come from the first two interactions, which are ionic. In solutions with \( \text{pH}<\text{pH}_{\text{PZC}} \) (in our case \( \text{pH}=3 \)), the oxide film will have a positive surface charge. The surface charge density due to acid-base properties of the oxide depends on the \( \text{pH}_{\text{PZC}} \) and, hence, the pH of the solution. This variation is calculated to be \( 2.0 \mu \text{C/cm}^2 \) per pH unit [57]. Thus, the excess of surface charge due to the acid-base properties of the passive films can be calculated when the \( \text{pH}_{\text{PZC}} \) is known. The calculated surface charge vs. pH for MgO and Al\(_2\)O\(_3\) is shown in Figure 4-18. This behavior is in agreement with the results reported for Al\(_2\)O\(_3\) by Kolics et al. [58].

Figure 4-18. Variation of the excess surface charge of the oxide layer as a function of pH
The adsorption of chloride ions is most favored on a positively charged oxide surface for which the ion-ion forces are attractive in nature. When the oxide is negatively charged, ion-ion forces are not attractive in nature so that the adsorption of Cl\textsuperscript{-} onto the negatively charged oxide surface is much less favored but can proceed through the effect of van der Waals forces. In contrast, negatively charged oxide surface favors the adsorption of Na\textsuperscript{+}. However for pitting to occur, it is necessary for the electrode potential to shift to more positive potential values until sufficient chloride is adsorbed on the surface and the critical pitting potential is attained. However in commercial aluminium alloys, the presence of precipitates on the metal surface greatly enhances localized corrosion attack in the presence of chloride ions. Nonetheless in the chloride adsorption effect, the electrode potential and chloride concentration in the solution may have a more important role in the control of the adsorption of chloride ions than the pH\textsubscript{PZC} parameter.

### 4.4.3 Mg enrichment in other aluminium alloys

Even though Mg surface enrichment has been shown to occur in Al-Mg alloys, this effect also appears in other aluminium alloy that include magnesium as minor or major alloying element. For instance, Figure 4-19 shows the magnesium enrichment effect for AA2024-T3, with a nominal composition of 4.38% Cu, and 1.45% Mg, as major alloying elements, in treated and untreated conditions. The natural oxide formed on the alloy shows that aluminium is the main constituent in the oxide composition. From the composition-depth profiles (CDP), it is evident that Mg and Cu do not contribute to the oxide formation. When the alloy is subjected to a sensitization temperature of 100\textdegreeC, Mg segregates to the oxide changing the composition of the interface whereas Cu concentration remains unchanged. This situation reflects the different activation energies for both elements and the energy needed for them to segregate to the oxide layer.
Mg surface enrichment can also be observed in the aerospace aluminium alloy AA7075-T6 with a nominal composition of 5.43wt%Zn, 2.4wt%Mg, and 1.53wt%Cu as major alloying elements. Figure 4-20 shows the composition depth profiles for this alloy. In this case, the natural oxide formed at room temperature is mainly composed of Al$_2$O$_3$ with a slight MgO contribution. Although copper and zinc are included in the alloy, they do not contribute to the room temperature oxide formation. When the alloy is subjected to a temperature of 100°C for 7 days, we can observe magnesium enrichment on the surface of about 3 times more than the initial concentration. From the composition depth profiles, we can state that Mg diffuses through the oxide occupying the outermost part of the layer. Once again, it is evident that
copper and zinc do not show any segregation to the oxide film and thus their contribution to
the formation of the oxide layer is null. These results obtained on the oxide composition
show that Mg in fact must have low activation energy of segregation. This situation indicates
that under low or moderate temperature, the metal oxide will modify its composition and,
depending on the temperature, its structure.

Figure 4-20. Auger concentration-depth profiles of AA7075-T6 in non-sensitized and
sensitized at 100°C for 7 days.
4.5 Conclusions

The oxidation in air of Al-Mg alloys and other selected aluminium alloys was explored to understand the factors affecting the oxide growth, composition as well as its behaviour in aqueous solution. In principle, the mechanism of the reaction that controls the oxidation of these alloys applies to most other aluminium alloys containing Mg as a major or as a minor alloying addition. The mechanism of enrichment was found to strongly depend on temperature and bulk Mg content of the alloyed metal. Activation energies for Mg segregation in Al₂O₃ were found to be in the range of 9.5 to 21.0kJ/mol. These activation energies reflect the easiness at which Mg ions move in Al₂O₃. In addition, the activation energy for Mg²⁺ in MgO was found to be 330kJ/mol. This situation indicates that once the MgO area in the oxide layer is formed, the mobility of Mg²⁺ is greatly damped preventing them from building a thicker MgO layer. Thus, the oxide layer on the Al-Mg alloy was found to reach a limiting thickness. Consequently for the layer to continue growing, it will be necessary to supply more energy to the Mg²⁺ ions. This situation can be easily achieved by increasing the temperature of the metal.

The electrochemical behaviour of Al-Mg alloys with enriched oxide layers was also found to experience chemical and structural transformations when immersed in aqueous solutions. These transformations depended on the characteristics of the aqueous solution. For instance in alkaline solution, the Mg enrichment on the surface suffers a hydration process that induces the formation of Mg hydroxide (Mg(OH)₂). This hydroxide compound is chemically stable in strong alkaline solutions forming a strong thick hydroxide layer that protects the surface of the alloyed metal. For solutions with neutral pH, a Mg(OH)₂ layer can be formed but due to the instability of this Mg compound in neutral solution, the hydroxide layer will dissolve exposing the Al oxide layer (Al₂O₃). This aluminium oxide layer will also transform forming a kind of Al hydroxide/oxide layer (AlOOH). This compound is very stable in neutral solutions forming a rather thick hydroxide/oxide layer that protects the alloyed metal. In the case of acid solutions, the Mg(OH)₂ layer can also be formed but it will be immediately dissolved. This effect induces a thinning of the Mg oxide layer until it dissolves completely exposing the Al₂O₃. Consequently, the Al oxide layer will hydrate producing AlOOH layer to
Composition of the oxide layer formed on 5XXX aluminium alloys

protect itself. Since the AlOOH is not stable in acidic solutions, the oxide/hydroxide layer will become thinner and thinner until the alloyed metal is exposed.

It is thought that Mg in the alloyed metal enhances the dissolution rate of the surface. Nonetheless, it was observed that after some time the Mg effect disappears making the surface oxide perform like Al₂O₃ oxide. The transients observed in the open circuit potential measurements suggested that the reactivity of the alloyed surface was caused by the preferential dissolution of MgO. Then, it is possible to conclude that when a Mg enriched alloy is immersed in an aqueous solution, the enrichment will have little or no effect on the corrosion rate of the metal.

4.6 References


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Chapter 5

Microstructure Characterization of 5XXX Aluminium Alloys

5.1 Introduction
Understanding the relationship between surface microstructure, electrochemistry and corrosion behaviour of commercial aluminium alloys has been a major area of research in the last decade [1, 2]. The metal surface has been considered the most important parameter for any corrosion process and at the same time the first line of defence against corrosion attack. It has also been established that localized electrochemical corrosion of aluminium alloys is primarily determined by the composition, size, and distribution of intermetallic compounds and, secondarily, by the properties of the solid solution of the alloyed matrix. In commercial aluminium alloys, the metal surface contains some physical inhomogeneities that cause a permanent distribution of anodic and cathodic sites that promote localized corrosion [3, 4]. These inhomogeneities are usually precipitates or impurities distributed on the surface of the metallic matrix. For this reason, the present chapter focuses on the understanding of the microstructure of commercial 5XXX Al-Mg alloys as well as identifying the type of intermetallics existing on the metal surface and their behaviour under prolonged sensitizing temperatures.

5.2 Experimental
The samples for Electron Probe Micro-Analysis (EPMA), X-ray elemental mapping, FE-SEM-EDX and micro-hardness characterization were ground with a 600 grit silicon carbide (SiC) paper and later mechanically polished down to 0.25µm. The sample preparation
removed between 500 to 800 µm of material from the metal surface. This particular sample preparation process permitted the elimination of the existing deformed layer induced by the fabrication process, typical of rolled products [5, 6]. Prior to the polishing process, the metal samples were sensitized in an air-circulating furnace at temperatures of 100°C and 200°C, each one for periods of 5, 11 and 30 days followed by air cooling until room temperature was achieved.

The samples prepared for Auger composition depth profiling (CDP) were first polished, cleaned, and later sensitized. This particular process provided additional information on the Mg surface enrichment occurring on less deformed and highly ordered surfaces. Samples used for electrical conductivity measurements were not mechanically polished, but rather they were used in their as-received form. In other words, the native oxide and deformed layer were left untouched. It is expected that the native oxide as well as the deformed layer does not affect the electrical conductivity measurements. The thickness of the deformed layer is reported to be of the order of 1 µm [5, 6]. The chemical composition of each Al-Mg alloy is given in Table 5-1.

| Table 5-1. Chemical composition of the Al-Mg alloys (wt%) |
|-----------------|---------|------|-----|-------|---------|------|-------|------|
| **Alloy**       | **Mg**  | **Mn** | **Si** | **Fe** | **Cu**  | **Cr** | **Zn** | **Ti** |
| AA5754          | 2.74    | 0.77  | 0.11 | 0.30  | 0.01    | 0.06  | 0.06  | 0.01  |
| AA5018          | 3.52    | 0.52  | 0.14 | 0.32  | 0.02    | 0.13  | 0.02  | 0.02  |
| AA5083          | 4.52    | 0.62  | 0.15 | 0.36  | 0.02    | 0.09  | 0.03  | 0.02  |

Auger composition-depth profiles (CPD) were performed on polished samples using the exactly the same experimental parameters used on ground samples (see details in Chapter 4). The system was calibrated to have an average sputtering rate of approximately 3nm/min (nanometers per minute) for Al₂O₃.

Micro-hardness measurements were performed with an Omnimet-MHT-Bueheler Vickers micro-indenter using a load of 100 grams. The resolution of this technique is in the order of +/- 4.0 HV₀.₁, maximum. A number of 30 measurements for each temperature and for each time of exposure were taken.
Electrical conductivity measurements were performed using the eddy current methods. The equipment used was a Sigmatest D-2.068 equipment. The apparatus resolution is in the order of +/- 0.04 mega siemens per meter (MS/m). The measurements were carried out on metal samples 2 cm wide by 10 cm long. The thickness varied for each alloy in the following way: for AA5754 the thickness was 5 mm, for AA5018 was 8 mm, and for AA5083 the thickness was 3.5 mm. The electrical conductivity (\(\sigma\)) is the reciprocal of the electrical resistivity (\(\rho\)) expressed mathematically as:

\[
\sigma = (\rho_{\text{total}})^{-1},
\]

where \(\rho_{\text{total}}\) is determined as

\[
\rho_{\text{total}} = \rho_t + \rho_i + \rho_d,
\]

where \(\rho_t, \rho_i,\) and \(\rho_d\) represent the individual thermal, impurity (alloying), and deformation resistivity contributions, respectively. The linear dependency of the thermal resistivity component (\(\rho_t\)) on temperature is due to the increase of thermal vibration and lattice irregularities with temperature, which serve as electron scattering centres. The impurity resistivity component (\(\rho_i\)) is related to the concentration of each impurity or alloying element in solid solution. Finally, the deformation resistivity component (\(\rho_d\)) is dependent on the plastic deformation. In other words, \(\rho_d\) increases as the number of dislocation increases. In the present work, the alloys employed for electrical conductivity measurements were not subjected to any kind of \textit{in situ} deformation. Since the alloys were used in the as-received condition (hot rolled until finished), a number of surface abnormalities as well as the presence of dislocations are expected to exist already in the alloys. Nonetheless, this number is assumed to remain constant since the relaxation of dislocations or other plastic deformations in the alloy is expected to take place at moderated temperatures. Relaxation for aluminium alloys occurs at temperatures above 300°C and, consequently, the contribution of the deformation resistivity component to variations of the electrical conductivity of the materials is discarded. Additionally, all electrical conductivity measurements were performed after the alloy reached room temperature, so no \textit{in-situ} thermal effects contributed to the resistivity of the metal. Therefore, most changes in the electrical conductivity are assumed to come from changes in the metal’s solid solution.
The characterization of the surface microstructure was performed by means of Field-Emission Gun Scanning Electron Microscopy (FEG-SEM JSM-6500F) coupled with an energy dispersive X-ray analyzer (EDX). In addition, element-composition mapping and quantitative-line scanning were carried out by means of Electron Probe Micro-Analysis (EPMA) JEOL-JXA 8900R. The microstructure characterization was focused on the type and composition of precipitates found on the metal surface, as well as additional changes induced by the sensitization treatment. The author does not intend to present an exhaustive classification of precipitates but rather a general overview of most relevant precipitates found on the alloyed metal surface. The element mappings consisted of a 100x100 grid covering an area of 50x50 µm. They were recorded using a 15 keV electron acceleration voltage and a beam current of 50 nA. For Mg, Al and Si the maps were made with the wavelength dispersive spectrometers (WDS). The recording time per pixel was 300 ms. for the samples sensitized for 5 or 11 days, and 500 ms. for the samples sensitized 30 days. The quantitative line scans were performed with a microprobe using an electron beam with energy of 15 keV and a current of 50 nA. The composition of the samples was determined from the x-ray intensities of the constituent elements Mg, Al and Si.

5.3 Results

5.3.1 Oxide composition of polished surfaces -Auger composition depth profiles-
Composition depth profiles (CPDs) were performed on polished samples in their unsensitized and sensitized conditions. The CPDs are shown in Figures 5-1 and 5-2. The profiles obtained on polished samples show differences with respect to the depth profiles obtained on ground sample: firstly, the degree of magnesium surface enrichment obtained on polished surfaces after sensitization is minor as compared to the degree of enrichment observed on ground surfaces (see Chapter 4). Secondly, the oxygen distribution throughout the thin oxide layer formed on polished samples appears to be less responsive to composition changes as a function of depth. As a result, the O²⁻ signal profile seems to be almost not affected by the concentration of Al³⁺ or Mg²⁺.
As previously stated in Chapter 4, the precise depth at which the oxide-metal interface exists cannot be clearly identified. For this reason, thickness of the oxide layer ($Z_o$) is defined as the mean depth sputtered at which the aluminium metal signal (Al) has risen to approximately 50% of its maximum value [7]. Comparing oxide thickness by this method, one should keep in mind that the value obtained is only an estimation since the sputtering rate changes with composition and depth. Differences in the sputtering yield between MgO (0.7) and Al₂O₃ (0.2) will be the most significant cause of variations in the sputtering rate [8]. Therefore, an average sputtering rate was estimated and set to 3nm/min.

For the non-sensitized low magnesium alloy AA5754 (Figure 5-1), the CPD shows that there is a minor magnesium enrichment in the natural oxide layer formed at room temperature. The thickness of the naturally formed oxide film is estimated to be 4.5 nm. Contrary to the composition depth profiles analyzed shown in Chapter 4, it is possible to observe that the oxygen signal appears to be less responsive to the fast decreasing concentration of $\text{Al}^{3+}$ or to the slight presence of $\text{Mg}^{2+}$ in the oxide layer. In other words, the oxygen signal does not show a marked decreasing profile as observed in non-polished alloy surfaces (Chapter 4). When the alloy is sensitized at 200°C (Figure 5-1), the magnesium enrichment increases from 8 to nearly 24 at% of the total oxide composition. For this sensitized alloy, the estimated oxide thickness is 6.7 nm. Once again, the oxygen signal in the composition depth profiles shows a quasi-constant oxygen distribution almost independent of the sputtered depth.
suggesting that the oxygen distribution throughout the layer is evenly distributed independent of the Al and Mg concentration. The intensity of the oxygen signal obtained during the depth profiles suggests that the oxide is a non-stoichiometric metal-deficient oxide. That is, the oxide film formed at these temperatures exhibits a deficiency of Al cations (a stoichiometric aluminium oxide implies an O/Al ratio = 1.5; a non-stoichiometric metal-deficient oxide implies an O/Al ratio > 1.5, whereas a non-stoichiometric metal-rich oxide implies an O/Al ratio < 1.5).

Figure 5-2. Composition-depth profiles of AA5083 (4.5 wt% Mg) in non-sensitized and sensitized condition. The surface of the treated metal was polished up to 0.25 µm and later sensitized.

In the case of alloys with higher Mg concentration AA5083 on the unsensitized condition shown in Figure 5.2, the trends of the Auger signal as a function of depth are similar to the trends observed for the unsensitized AA5754. The contribution of Mg to the formation of the oxide layer is minimal. In addition, the oxygen signal across the oxide layer shows only a small variation as a function of depth going from 40% at the surface to a maximum concentration of 45% and later slowly decreasing to 35%. For the sensitized alloy AA5083 (Figure 5-2), the depth profile shows an increase contribution of magnesium to the formation of the oxide layer. The same alloy with the same bulk Mg content and the same treatment parameters but with a ground surface (600 grit-SiC) can get a higher Mg enrichment (20% more) than polished samples. This result suggests that surface characteristics (e.g. surface roughness and degree of surface deformation) play an important role in the surface
enrichment mechanism. Contrary to the behaviour observed for the unsensitized AA5083, the oxygen signal shows a slowly decreasing behaviour as depth increases for the sensitized alloy. In this case, the oxygen signal follows a similar trend as the one observed on ground alloys.

As mentioned before, the intensity of the oxygen signal suggests the formation of a predominantly metal-deficient oxide. These observation correlate fairly well with the results obtained by Jeurgens et al. [9]. They found that for temperatures ($T$) below 300°C, an aluminium-deficient amorphous oxide film of limiting thickness is developed, whereas for higher temperatures ($T > 300°C$), an Al-enriched amorphous oxide film is formed which gradually attains the stoichiometric composition of $\text{Al}_2\text{O}_3$ and becomes crystalline $\gamma$-$\text{Al}_2\text{O}_3$.

5.3.2 Effects of sensitization treatment on the bulk magnesium concentration as a function of temperature - microhardness and electrical conductivity-

Figure 5-3 shows the effects that sensitization have in the micro-hardness of the alloyed metal as a function of time at 100°C and 200°C, respectively. The micro-hardness for the alloys at time equal to zero ($t = 0$) corresponds to the unsensitized metal. At 100°C, the alloy with low Mg content (AA5754) displays a decreasing behaviour in hardness going from 76.23 HV$_{0.1}$ to 71.80 HV$_{0.1}$ after 30 days of sensitization (720 hours). A similar behaviour is observed for the AA5018 (3.5% Mg) going from 87.80 HV$_{0.1}$ to 84.70 HV$_{0.1}$ after 30 days of sensitization at 100°C. In the case of AA5083 with 4.5%Mg, the micro-hardness appears to decrease at a slower rate going from 92.30 HV$_{0.1}$ to 90.00 HV$_{0.1}$. This particular trend falls within the experimental error.

At 200°C, the alloy AA5754 shows within 5 days a fast decrease from 76.23 HV$_{0.1}$ to 69.86 HV$_{0.1}$. After this period, the alloy maintains a constant value of approximately 69.62 HV$_{0.1}$. In the case of AA5018, the alloy displays a rather interesting behaviour. Its micro-hardness displays a decrement from 88.00 HV$_{0.1}$ to 87.20 HV$_{0.1}$. However due to the large error-margin of each measurement, the micro-hardness trend might well be constant. Hence, the effect of sensitizing this alloy (AA5018) at 200°C for prolonged sensitizing times may be limited.
Figure 5-3. Micro-hardness as a function of sensitizing time for Al-Mg alloys with different bulk Mg-concentrations treated at 100°C and 200°C.
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For AA5083 (4.5%Mg) shows a small decrease on the micro-hardness within the first 24 hours of sensitization from 92.22 HV\textsubscript{0.1} to 90.40 HV\textsubscript{0.1}. After this period of time, the alloy’s micro-hardness starts to display a slower change rate going from 90 HV\textsubscript{0.1} to 88.60 HV\textsubscript{0.1} after 30 days of exposure to 200°C. It is possible to see that most marked changes in terms of micro-hardness are observed in the alloy with low Mg content (AA5754), whereas the alloy AA5018 with 3.5%Mg content shows minimum response to the sensitization treatment, especially at 200°C.

Electrical conductivity measurements were performed for Al-Mg alloys with different Mg bulk content. Figure 5-4 displays the electrical conductivity behaviour of alloys AA5754, AA5018 and AA5083, subjected to two sensitizing temperatures: 100°C and 200°C. The electrical conductivity observed for AA5754 within the first 8 days display a well-defined ascending behaviour dependent of the sensitizing temperature. AA5754 shows at 100°C an increase in the electrical conductivity from 20.23 to 20.36 MS/m (mega-siemens per meter) as time of exposure increases. When the alloy is exposed to a sensitizing temperature of 200°C, the changes observed in the electrical conductivity are immediately evident. Within the first 5 days of exposure, the conductivity increases from 20.23 to 20.33 MS/m. From this period to the end of the 30 days treatment, the conductivity slowly rises to a value of 20.36 MS/m.

The AA5018 with 3.5%Mg content displays a rather unusual behaviour. The electrical conductivity for this alloy appears to decrease within the first 11 days of exposure for both sensitizing temperatures. After 14 days, the alloy sensitized at 100°C shows an increase in electrical conductivity to 17.96 MS/m. When the alloy is sensitized at 200°C, the electrical conductivity also displays a decreasing behaviour within the first 23 days of exposure going from 17.93 to 17.88 MS/m. After this period, the electrical conductivity shows a slight increase reaching a value of 17.90 HV\textsubscript{0.1}. This unusual behaviour may be due to the dissolution of Mg-rich precipitates contribute to increase the amount of Mg in solid solution and, hence, decreasing the electrical conductivity of the alloy. However, the decrement in conductivity may also be induced by the formation of coherent and semi-coherent precipitates increasing the scattering effect [10, 11]. Nonetheless, the magnitude of the electrical conductivity changes observed in these two alloys may be considered minor.
Figure 5-4. Electrical conductivity for alloys with different Mg Bulk content as function of sensitizing time and temperature.
For the alloy AA5083 with 4.5% Mg content (Figure 5-4), the electrical conductivity seems to have a more noticeable variation. At 100°C, the alloy experiences a slight increase in conductivity reaching a plateau of 16.70 MS/m after 11 days of exposure. From this point, the electrical conductivity of the alloy remains unchanged independent of the sensitizing time. In contrast, when the alloy is sensitized at 200°C, the electrical conductivity shows a marked ascending behaviour as a function of sensitizing time. This ascending behaviour indicates that the sensitized alloy is losing Mg from solid solution.

The effect that Mg in solid solution has on the electrical conductivity of the alloy can be clearly seen in Figure 5-5. As previously mentioned, magnesium has a high solid solubility in aluminium at high temperatures (up to 14.9 wt% at 450°C). Its solubility decreases to approximately 1.7 wt% at room temperature but the rate of decomposition of the supersaturated solid solution is rather low [12]. By increasing the amount of magnesium in solid solution of the alloy, the mechanical strength of the alloy increases following a quasi-linear relationship [12, 13]. Contrary to this behaviour, the electrical conductivity for unsensitized alloys decreases as a function of bulk Mg-content.

![Electrical conductivity (unsensitized)](image-url)

**Figure 5-5.** Electrical conductivity of Al-Mg alloys as a function of Mg content.
5.3.3 Precipitation near grain boundary area -FEG-SEM/EDX-

Precipitation plays an important part in the localized corrosion process of aluminium alloys. The role of precipitates in this electrochemical process is bounded by their size and composition as well as their location (grain boundary vs. grain interior). Therefore, it is important to have a general knowledge of the type of precipitates existing in the alloy, their size and most common location in the alloy. However, the principal aim of the author is to only give a general overview of existing precipitates and identify the ones that are more relevant in our research.

The identification of precipitates (type and composition) was carried out in commercial unsensitized Al-Mg alloys by means of FEG-SEM and EDS. The analysis was performed on three samples with different Mg contents. On these samples, the dominant number of precipitates were selected for composition analysis and later compared to the precipitates found on the other two remaining alloys.

Figure 5-6. SEM micrograph with its corresponding EDX spectrum (point 1) of a possible Mg$_2$Si precipitate. Point 2 shows the spectrum of the alloyed matrix.
The first relevant particle observed is shown in Figure 5-6. With the presence of Si as a minor alloying element, Mg can form Mg$_2$Si precipitates. This precipitate is characterized for having a dark colour with a size rarely exceeds 5µm in length. The solubility of this phase is small so certain amount may remain out of solid solution and visible in wrought products. These types of precipitates are important because they are electrochemically active with respect to the aluminium matrix [14]. However, their location is most of the time in the grain interiors limiting his role in the localized corrosion process to potential sites for pits.

Figure 5-7. SEM micrograph with its corresponding EDX spectrum of Si-rich particles and Al(Mn,Fe,Cr)Si intermetallics.

Figure 5-7 shows other type of precipitates that are found in the alloy. EDX spectra, taken in point 1, show that these small precipitates are Si-rich particles, indicated by the higher amount of counts compared to the counts observed for the Mg signal. The average size of these Si-rich precipitates is around 500nm but they never exceed 800nm. They are randomly distributed throughout the grain, most of the time in grain interiors but occasionally near the grain boundary. Si-rich precipitates are electrochemically active with respect to the matrix.
(point 1). In other words, they can induce dissolution of the surrounding matrix. Due to their size, location and composition, they can become potential sites for pitting as well as potential starting sites for intergranular corrosion.

Point 3 (Figure 5-7) indicates the composition of larger intermetallics found of the surface of the Al-Mg alloys. These precipitates are identified as quaternary phases (Mn,Fe,Cr)Si or ternary phases (Mn,Fe,Cr). These particles are reported to be electrochemically passive with respect to the aluminium matrix [15] and are found most of the time at triple points and grain boundaries. Their size varies from 5 µm to 20 µm in length. However, their potential role in the intergranular corrosion process is negligible [16].

It should be pointed out that the counts for the aluminium and magnesium signal are always important in the EDX spectra. This is due to the fact that the background signal of the matrix always affects the EDX spectra. The depth of penetration of the EDX electron beam is a few microns, which is comparable with the size of the intermetallics. In a similar way, the Mg in solid solution might contribute to the peaks of the spectra. This situation can be seen in point 1 in Figure 5-7 and in point 2 in Figure 5-8 where Si-rich particles show a small Mg peak. This Mg peak might be a contribution of the Mg from the solid solution.

Besides identifying Al(Mn,Fe,Cr)Si intermetallics as well as Si-rich particles, Figure 5-8 also shows grain boundary dissolution, a situation frequently found in polished Al-Mg alloys. EDX composition analysis was taken in two points: on the grain boundary (point 3) and on the grain interior (point 4). By superimposing the spectra of these two points, it is possible to observe a variation of the magnesium content along the grain boundary. However, the difference between the two Mg signal (approximately 300 counts) is rather small to be conclusive. Nonetheless, Zhou et al. [17] reported grain boundary enrichment on AA5182-O alloy with 4 wt% Mg content, by employing energy dispersive x-ray (EDX). The difference between the Mg grain boundary signal and the bulk grain signal reported by Zhou is in the order of 25 counts, which is much smaller than the difference obtained in Figure 5-8. Therefore, the magnesium enrichment observed with the FEG-SEM may after all be meaningful.
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Figure 5-8. SEM micrograph with its corresponding EDX spectrum Al(Mn,Fe,Cr)Si and Si-rich precipitates indicated by point 1 and 2, respectively. Points 3 and 4 show a possible Mg enrichment of the grain boundary (point 3) compared to the grain interior (point 4).

There are differences in respect of the number of particles of each type present on the surface; the most abundant are Al(Mn,Fe,Cr)Si or Al(Mn,Fe,Cr) particles, whereas (Al,Mg) possibly β-phase and (Al,Mg,Si) particles are the least numerous. In addition, the existence of Si-rich particles has also been confirmed. In order to make a more accurate assessment on the type of intermetallics existing on the surface and the effects that sensitizing produces on the amount of precipitates, elemental mapping was performed focusing on Al, Mg and Si elements.
5.3.4 Surface precipitation as a function of time -Electron Probe Microanalysis (EPMA) and X-ray elemental mapping-

The composition analysis of precipitates found in Al-Mg alloys was determined with Electron Probe X-ray Micro-Analysis (EPMA). Elemental mapping was performed on samples in order to reveal the distribution of the alloying elements that could lead to a higher probability of finding \( \text{Mg}_2\text{Al}_3 \)-particles (\( \beta \)-phase). As previously mentioned, the maps consisted of a 100x100 grid covering an area of 50x50 µm. The maps were made with the wavelength dispersive spectrometer (WDS). A Secondary (SEI) and a Backscatter Electron Image (BEI) were obtained for the samples in order to reveal the morphology of the alloys.

Although Al(Mn,Cr,Fe) phases could contribute to the corrosion process in commercial Al-Mg alloys in the form of pitting corrosion, they do not contribute to the intergranular corrosion process. For this reason, Mn, Fe and Cr are disregarded from the elemental mapping. Only Mg, Al and Si were the main elements traced in the elemental mapping. As previously mentioned, precipitates such as \( \beta \)-(\( \text{Al}_3\text{Mg}_2 \)) phases, Al(Mg,Si), and \( \text{Mg}_2\text{Si} \), as well as Si-rich phases are most of the time found at or near the grain boundaries. Due to their small size, location and composition, their role in the intergranular corrosion process is potentially important [14, 18]. Type of the alloy and extend of the sensitization treatment applied to the samples are described in Table 5-2.

### Table 5-2. The sample designation belongs to different experimental conditions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sensitation temperature (°C)</th>
<th>Sensitation time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5754</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>AA5754</td>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>AA5754</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>AA5018</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>AA5018</td>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>AA5018</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>AA5083</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>AA5083</td>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>AA5083</td>
<td>100</td>
<td>30</td>
</tr>
</tbody>
</table>
The aim of the mappings is to visualize the distribution of these precipitates and at the same time monitor the effects that prolonged sensitizing times have on these precipitates. Figure 5-9 illustrates the backscattered image of the alloy AA5754 after 5 days of treatment at 100°C. Mg-rich precipitates -possibly Mg$_2$Si- (identified as dark colour particles) and Si-rich precipitates (identified as bright colour particles) appear randomly distributed on the surface. In addition, Figure 5-9 also shows the elemental maps for Al, Mg and Si. A white box drawn in the backscattered image indicates the area where the elemental maps were performed. Dark blue colours in the elemental map indicate absence or low element concentration, whereas light pink tending to white colours indicates high element concentration. From the backscattered image in Figure 5-9, it is evident that a high amount of silicon-rich precipitates (bright particles) outnumber the Mg-rich precipitates (dark particles) after 5 days of sensitization. As the sensitizing treatment progresses to 11 days (Figure 10), most of the Mg-rich particles seem to disappear from the metal surface yielding a predominance of the Si-rich particles. After 30 days of sensitization (Figure 11), the metal surface shows a strong reduction of Mg-rich precipitates and a rather small decrease of Si-rich particles.

Elemental maps for the AA5754 alloy provide additional information on the transformation that precipitates experience. The maps, shown in Figure 5-9, illustrate the Mg distribution in the bulk metal without visible precipitation, whereas the Si mapping indicates that Si-rich precipitates are formed within 5 days of exposure at 100°C. After 11 days (Figure 5-10), Mg in solid solution decreases inducing the initial formation of Mg-rich and Mg$_2$Si phases. At the same time, Si-rich particles seem to decrease in number on the metal surface. At the end of 30 days of exposure (Figure 5-11), Mg in solid solution is modified inducing the formation of finer and smaller Mg-rich precipitates along with the formation of few Mg$_2$Si precipitates along with fine Si-rich particles. Although it is possible to visualize the formation of Mg-rich and Si-rich particles, elemental mapping does not show any delineation of grain boundaries due to precipitation.

For AA5018 alloys with 3.5%Mg content, the behaviour seems to follow the same pattern as the alloy with lower Mg content. Figure 5-12 show the backscattered image as well as the elemental mapping of AA5018 after being sensitized at 100°C for 5 days. As before, the Mg mapping shows the existence of a small amount of Mg-rich precipitates plus larger Si-rich
particles. The density of Si-rich precipitates appears to be dominant among all the precipitates found on the metal surface. As the sensitizing time increases to 11 days (Figure 5-13), the formation of Mg₂Si or Al(Mg,Si) phases is observed. Additionally, this situation correlates with the coarsening of Si-rich particles present in the alloyed metal increasing their size and consequently reducing the number of this type of precipitates. In the Si map, this particular situation is evident. Few precipitates have recombined with Mg to form Mg₂Si or Al(Mg,Si) phases reducing, at the same time, the number of Si-rich precipitates (see Si map in Figure 5-14). After 30 days of exposure, the increase in the number of fine Mg₂Si as well as Al(Mg,Si) particles can be seen on the metal surface (Figure 5-14). However, a large number of these new particles can be classified as Si-rich precipitates. The Si mapping, shown in Figure 5-14, illustrates the increase number of fine Si-rich particles of approximately 1 to 2 µm in length.

Figure 5-15 shows the microstructure of AA5083 aluminium alloy sensitized at 100°C for 5 days. The backscattered image in Figure 5-15 illustrates the clear dominance of Si-rich precipitates (bright particles). This fact is also confirmed in the elemental mapping for silicon. Very few Mg-rich can be seen on the surface. The Mg map also shows the very small formation of particles of this type. In the map only 4 possible Mg-rich precipitates are visible in an area of 2500 µm². After 11 days of treatment (Figure 5-16), the number of Si-rich precipitates appears to increase in number. The backscattering image shows larger size particles have formed on the surface. The Si-mapping shows the formation of fine Si rich precipitates but only few of them have recombined with Mg to form Mg₂Si or Al(Mg,Si) phases. Finally, at the end of 30 day of treatment at100°C (Figure 5-17), the alloy shows even more Si-rich precipitates randomly distributed over the entire surface. In fact, Si mapping shows the formation of large and small Si-rich precipitates. In contrast, the number of Mg-rich particles has slightly increased in the form of fine particles with sizes in the range of 2 µm or less. It is interesting to see that even Si is a minor alloying element, usually present in the range of 0.15wt% or less, can induce a larger number of fine precipitates usually in the range of 1 to 3 µm.
Figure 5-9. Back-scattered electron image of AA5457 sensitized at 100°C for 5 days showing Mg-rich particles (dark) and Si-rich particles (bright). A white box indicates the location of the area for elemental mapping of the Al-K\(\alpha\), Mg-K\(\alpha\), and Si-K\(\alpha\) line.

Figure 5-10. Back-scattered electron image of AA5457 sensitized at 100°C for 11 days showing Mg-rich particles of Mg\(_2\)Si (dark) and Si-rich particles (bright).
Figure 5-11. Back-scattered electron image of AA5457 sensitized at 100°C for 30 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).

Figure 5-12. Back-scattered electron image of AA5018 sensitized at 100°C for 5 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).
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Figure 5-13. Back-scattered electron image of AA5018 sensitized at 100°C for 11 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).

Figure 5-14. Back-scattered electron image of AA5018 sensitized at 100°C for 30 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).
Figure 5-15. Back-scattered electron image of AA5083 sensitized at 100°C for 5 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).

Figure 5-16. Back-scattered electron image of AA5083 sensitized at 100°C for 11 days showing Mg-rich particles of Mg$_2$Si (dark) and Si-rich particles (bright).
5.3.5 Surface precipitation - EPMA line scans-

For all Al-Mg samples one quantitative line-scan was performed with the primary aim to look for changes in composition that may lead to the identification of Mg$_2$Al$_3$-particles at grain boundaries as well as possible magnesium enrichment. The line scanned comprised of 100 point in a line of 100 µm in length. Figure 5-18 illustrates the grains size and grain boundary precipitation found in a commercial Al-Mg alloy. It is evident from Figure 5-18 that a line-scan of 100 µm will certainly include several grain boundaries as well as number of precipitates existing at the grain boundaries.

β-phase precipitates are reported to nucleate and grow at the grain boundaries. Formation of this phase in grain boundaries depends on the bulk Mg content of the alloy. In other words for alloys with low Mg content ([Mg] < 3.5wt% means magnesium remain mostly in solid solution), low precipitation of β-phase particles can take place but they may be dispersed uniformly throughout the matrix. In contrast, when the bulk Mg content exceeds 3.5wt%
(supersaturated solid solution), heavy grain boundary β-phase precipitation occurs with little or none precipitation within the grains. If these precipitates form a continuous network in the grain boundaries, a strong Mg signal in the EPMA line-scan can be detected.

![Figure 5-18](image.png)

Figure 5-18. Light optical microscope picture of an Al-Mg alloy sensitized for 11 days at 100°C. The surface was etched with Nitric acid for 3 hours in order to reveal the grain boundaries and the density of grain boundary precipitation.

Figures 5-19 to 5-21 show the results obtained by EPMA line-scanning (indicated by an arrow on the backscatter images of Figures 5-9 to 5-17) of the sensitized alloys. Aluminium depleted regions in the line scans indicate the presence of precipitates as well as possible enrichment of alloying elements. For instance, it is possible to observe places where Mg and Si peaks show a maximum while in the same place the aluminium signal displays a minimum peak representing aluminium depletion. This situation indicates composition changes mainly due to the presence of precipitates confirmed by the width of the signal’s peak that correlates with the size of precipitates. However, it is necessary to keep in mind that any possible enrichment of alloying elements would be much more difficult to discriminate among Si-rich or Mg-rich precipitates. In addition, the detection of β-phase particles in grain boundaries may represent an extra drawback to the line-scan technique since the size reported for these particles ranges between 50 nm to 1 µm. Nevertheless, the line-scans can provide additional information on the effects that extended sensitizing periods cause to the metal surface in commercial Al-Mg alloys.
Figure 5-19. The EPMA composition line-scans of the alloyed surface along the line indicated by an arrow in the backscatter images shown in Figure 5-10, 5-11, and 5-12 for sensitized AA5754 alloy.
Figure 5-20. The EPMA composition line-scans of the alloyed surface along the line indicated by an arrow in the backscatter images shown in Figure 5-13, 5-14, and 5-15 for sensitized AA5018 alloy.
Figure 5-21. The EPMA composition line-scans of the alloyed surface along the line indicated by an arrow in the backscatter images shown in Figure 5-16, 5-17, and 5-18 for sensitized AA5083 alloy.
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The results obtained for the alloy AA5754 (2.7wt%Mg) sensitized at 100°C for periods of 5, 11, and 30 days are shown in Figure 5-19. The line-scans for this alloy after 5 day of sensitization show a high density of Si peaks, while the Mg peaks observed are minimal. Few of these peaks coincide with each other suggesting the formation of few Al(Mg,Si) particles. However, it is evident that the dominant precipitated phases found on the metal surface are Si-rich particles. Sizes of Si-rich particles range from 2 µm to 5 µm in length. After 11 days of sensitization at 100°C (Figure 5-19), the number of Si peaks decreases while the number of Mg-rich peaks remains, in average, the same. However, it is observed that the strength of the Mg signal increase indicating that some precipitates became richer in Mg content. Particles such as Mg2Si and Al(Mg,Si) can be clearly identified. At the end of 30 day of sensitizing treatment, the number and strength of Si-peaks has noticeably decreased. The Mg signal also shows a similar trend as the one observed for the Si-signal exhibiting a series of small low-strength peaks. This situation indicates the formation of fine Al(Mg, Si) particles, a couple of Si-rich precipitates as well as the formation of Mg-rich precipitates possibly of the Al3Mg2 type.

Figure 5-20 shows the effects that extended periods of sensitization bring to the AA5018 alloy (3.5wt%Mg). Immediately, it is possible to observed a similar effect as the one described for alloy AA5754 regarding the number, size and composition of precipitates as function of time. That is after 5 days of sensitization, the number of Si-peaks prevail over the Mg-peaks obtained in the line-scan. In other words, a high number of Si-rich precipitates are observed compared to the Mg-rich precipitates. Few Al(Mg, Si) particles are visible but the surface seems to be dominated by S-rich precipitates. After 11 days, the number of Si peaks slightly decreases while the Mg-peaks show only a modest increase in the strength of the signal (Mg concentration). Also, it is possible to observe the formation of few Mg2Si particles adds up to the already existing amount of Al(Mg, Si) particles. Nevertheless, Si-rich particles continue to dominate the type of precipitates found on the metal surface. Finally, after 30 days of sensitization (Figure 5-20), the number of Si-peaks decreases but the signal strength appears to grow indicating an increase of Si content on precipitates. In a similar way, the number of Mg-peaks appears to remain constant while the strength of the signal increases. The line-scan shows the formation of Mg2Si, Al(Mg, Si) and even Si-rich particles. However, the formation of Mg-rich particles appears to be minimal.
In the case of the alloy AA5083 with 4.5wt%Mg content, the formation of Mg rich precipitates appears to be small after 5 days of sensitization. A similar result is observed for the Si-signal. Only one strong Si-peak can be seen in Figure 5-21. Peaks observed in the Al-signal combined with depletion peaks in the Mg-signal may indicate the presence of Al(Mn,Fe) particles. In a similar way after 11 days of exposure to 100°C, the line-scan shows only two strong peaks on the Si and Al signals, and one depletion peak observed in the Mg signal. This combination of peaks indicates that the particle may be an intermetallic of the type Al(Mn,Fe)Si. The size of this intermetallic is estimated to be in the range of 10µm. Finally after 30 days of sensitization, it is possible to observe the appearance of a large Mg<sub>2</sub>Si particles of approximately 10µm in length as well as smaller particles of the same type. Additionally, Si-rich and Al(Mg,Si) particles can also be identified. In most of EPMA line-scans, the detection of Al<sub>3</sub>Mg<sub>2</sub> precipitates in grain boundaries as well as possible Mg enrichment is difficult and may require, after all, a different surface technique.

5.4 Discussion

Auger composition-depth profile analysis performed on polished samples (Figures 5-1 and 5-2) show that the native oxide comprises of a slight Mg enrichment that contributes to the formation of the oxide. However, the degree of enrichment measured on polished surfaces, sensitized and unsensitized, is smaller than the enrichment observed on unpolished samples (see Chapter 4). These results suggest that the magnesium enrichment in the oxide layer greatly depends on the microstructure of the metal surface and near-surface. In other words, alloys with highly deformed surfaces are shown to have a stronger Mg enrichment than on highly flat (mirror-like) surfaces. During the grinding process, the alloyed surface is deformed and material is removed by the abrasive grains of the grinding paper. After the surface is ground, a highly deformed layer is formed on the near-surface [19]. The thickness of this deformed layer strongly depends on the grain size of the grinding paper as well as the characteristic of the ground material (hard vs. brittle) as shown by Hegemans [19]. The deformed layer, in many ways, is similar to the deformed layer obtained during the rolling process of wrought aluminium alloys [20]. On both cases, the Mg enrichment obtained on the surface is strong (see Chapter 4 and reference [22]). In contrast, the deformed layer on
polished surfaces is almost non-existent. Even though mechanical polishing induces a sort of surface deformation, this deformation is considered to be negligible. Hence, the Mg enrichment measured on this type of surfaces is minimal compared to ground surfaces. Similar results have been reported for single crystal Al-Mg alloys by Esposto et al. [21], and for polycrystalline Al-Mg alloys reported by Holub et al. [22].

Extended periods of exposure to moderated temperatures (usually in the range of 70 to 200°C) produce changes in the mechanical properties of the Al-Mg alloys. These changes are presented in terms of micro-hardness and electrical conductivity (Figures 5-3 and 5-4) both as a function of time and as a function of temperature. Results obtained show that the micro-hardness of the alloy is dependent on the Mg content of the alloy and, in less degree, on the sensitizing temperature that the alloy is subjected to and on the duration of the exposure to this temperature. It is evident that stronger changes on the micro-hardness are observed for low Mg content alloys (e.g. AA5754), whereas smaller changes are observed for alloys with higher Mg content (e.g. AA5083). In addition, on low Mg content alloys, temperature shows to be a parameter that dictates how fast the changes take place. At lower temperatures, the observed changes in the micro-hardness will be slow, while at higher temperatures the changes will occur at a faster rate.

In terms of electrical conductivity, the results obtained show also dependency on the Mg content and, in less degree, on the temperature applied to the alloy. Low Mg content alloys show smaller changes on their electrical conductivity than for alloys with higher Mg content. In other words, the effects that prolonged sensitizing treatments have on the alloy are much more marked on alloys with higher Mg content. It is interesting to see that the AA5018 (3.5wt% Mg) alloy appears to have minimum response to prolonged exposures to moderated temperatures.

In general, it is evident the trend between the micro-hardness and the electrical conductivity both as a function of Mg content in the alloy: For low Mg alloys, their micro-hardness is low while the electrical conductivity for the same type of alloys is high. When the Mg content in the alloy decreases, the micro-hardness and electrical conductivity appear to get closer to the values of AA1050 alloy (99.95% Al). On the other hand, as the Mg content in the alloy
increases, the micro-hardness increases while the electrical conductivity decreases. This behaviour is illustrated in Figure 5-22 for alloys with different bulk magnesium content at room temperature. This trend is expected since Mg is the strengthening factor in the AA5XXX series. Consequently, variations on the Mg content in solid solution will cause changes on the mechanical properties of the alloy as well as its electrical conductivity. During prolonged exposures to moderate temperatures, the alloy shows a similar trend as a function of time. In other words, for a fixed temperature, the micro-hardness of the alloy starts decrease as the time of exposure increases. At the same time, the electrical conductivity shows an ascending behaviour as the time of exposure increases. How fast the changes take place is determined by the sensitizing temperature and by the initial Mg content of the alloy.

Figure 5-22. Influence of the bulk magnesium content on the micro-hardness and electrical conductivity properties of the alloy at room temperature.

The ascending and descending behaviour of the micro-hardness and electrical conductivity, shown in Figures 5-3 and 5-4, are a clear sign that the bulk Mg content is experiencing an important variation. It appears like the alloyed metal is losing magnesium from the bulk content. These results correlate with the degree of Mg enrichment that the surface of the alloyed metal experiences. Certainly, the grain boundary area should also be enriched. This
enrichment on grain boundaries should be reflected in the form of heavy precipitation of Mg-rich particles and/or heavy concentration of Mg as solute-free atoms. It is important to keep in mind that alloys with Mg content below 3.5wt% are considered to have Mg completely or almost completely in solid solution and, consequently, the formation of Mg-rich particles (β-phase: Al₃Mg₂ or Al₈Mg₅) is uniformly distributed over the metal surface. In contrast, when the bulk Mg content exceeds 3.5wt%, the solid solution of the alloy is considered to be supersaturated. As a result, the formation of Mg-rich precipitates is found to be concentrated mainly on grain boundaries.

The results obtained indicate that particles such as the ones detected by FEG-SEM, and EPMA can be arranged in the following groups:

- **Group 1:** Al, Mn, Fe, Cr and occasionally combined with Si
- **Group 2:** basically comprising Al, Si, Mg
- **Group 3:** mainly containing Al and Mg

Intermetallics such as Al(Mn,Cr,Fe) and Al(Mn,Fe) are found to be between 5 µm to 20 µm in length and their location on most occasions is in the path of the grain boundaries. As an example of this situation, Figure 5-18 illustrates the grain boundary lines and a number of large intermetallics (gray particles) that belong to group 1. Almost all of them are located at grain boundaries and triple points. Despite of their location, this type of particles is not reported to contribute to the intergranular corrosion process [17]. At most, they contribute to localized corrosion in the form of particle induced pitting. Moderate temperatures and prolonged exposures to these temperatures do not appear to inflict any effect on these intermetallics.

In contrast, intermetallics in group 2 which includes Al(Mg,Si), Mg₂Si as well as Si-rich phases are also found at or near grain boundaries. Their size varies between 1/2µm to 5 µm. Elemental mappings and line scanning help to visualise how prolonged exposures to moderated temperatures affect this type of precipitates. These results also indicate that extended exposure affect mainly the Mg content in the particle and, consequently, its size. In addition, prolonged exposures favour the formation of fine Si-rich particles on the metal surface.
It is important to point out that delineation of grain boundary lines due to either Mg enrichment or Mg-rich precipitates in the form of $\beta-(\text{Al}_3\text{Mg}_2)$ phase was not detected by the elemental mapping. Nonetheless, this lack of detection does not suggest that grain boundary precipitation or Mg enrichment does not take place. On the contrary, the results may suggest that the detection of grain boundary enrichment or precipitation or a combination of both may occur at the submicron level and consequently a better sample preparation and a better detection technique may be required.

5.5 Conclusions

Prolonged exposure to moderated temperatures such as 100°C and 200°C induce changes in the properties of Al-Mg alloys. These changes are:

- Low Mg content alloys display a stronger response to micro-hardness changes induced by temperature and time of exposure.
- Stronger electrical conductivity variations are observed on alloys with higher Mg content.
- In both cases, electrical conductivity and micro-hardness indicate that the Mg content in the alloy decreases.
- Prolonged exposures to moderated temperatures affect mainly precipitates containing magnesium and silicon. It is observed that long periods of exposure increase the number and size of Si-rich and (Mg, Si) particles.
- Al(Mn,Fe,Cr) or Al(Mn,Fe,Cr)Si particles dominate the type of precipitates found in commercial Al-Mg alloys. In second place are Si-rich and (Mg, Si) precipitates (except Mg$_2$Si which are rarely found in the alloy).
- Si rich precipitates are also found to be present near the grain boundaries.

Grain boundary lines due to either Mg enrichment or precipitation in the form of $\beta-(\text{Al}_3\text{Mg}_2)$ phase particles were not detected by the elemental mapping. This lack of detection may suggest that grain boundary enrichment or precipitation (or a combination of both) occurs at
the submicron level and consequently a better sample preparation and detection technique may be required.

5.6 References

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Chapter 6

Role of magnesium in the intergranular corrosion process of 5XXX aluminium alloys

6.1 Introduction

The AA5XXX alloys are generally known for their excellent corrosion resistance. This particular property makes them widely popular for various applications involving corrosive environments. However, these alloys can become susceptible to intergranular corrosion (IG) attack and intergranular stress corrosion cracking (IGSCC) when exposed to temperatures ranging from $50^\circ C$ to $200^\circ C$ for extended periods of time. A combination of temperature and aggressive environment can potentially bring negative effects to these alloys during service conditions.

Al-Mg alloys are commonly being used in marine, rail and rigid packaging applications and none of these areas are such that the potential for sensitization is a significant concern. However, there is a growing utilization of AA5XXX alloys for automotive and structural application where the alloys could face sensitizing temperatures. For instance, the center for nuclear energy studies in Belgium, dedicated to test different materials for nuclear reactors, has tested the alloy AA5754 (2.7wt% Mg) in a pilot water reactor. It is important to point out that the AA5754 alloy is considered one of the most corrosion resistant alloys in the 5XXX series. This alloy was used in plate-form (approximately 1 to 2 mm thick) as the cladding of fuel reservoir in a test reactor. During irradiation, the water reactor induced a heat flux of 520Watts/cm$^2$. In this way, the alloyed plate heated up until reaching a temperature of 160-180$^\circ C$ at the surface. This temperature remained nearly constant for a period of 2 years (the trial period for the pilot water reactor). Almost at the end of the trial period, technicians of the nuclear energy center observed that parts of the AA5754 cladding were partially gone.
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After performing surface analysis on the affected metal surface, heavy intergranular corrosion attack was found. Another example is the alloy AA5182 (4wt% Mg). This alloy has been reported to suffer similar problem in service conditions after been exposed to a temperature of 70°C for 1000 hours in a humid environment [1,2]. These examples clearly illustrate that, when any Al-Mg alloy is subjected to moderate (or high) temperatures for a prolonged period of time in humid environments, intergranular corrosion will inevitably take place. Many other potentials applications for AA5XXX alloys could involve exposure to elevated temperatures in corrosive environments. Consequently, the issue of sensitization of Al-Mg alloys in service conditions becomes very important.

Intergranular corrosion and stress corrosion cracking (SCC) susceptibility of Al-Mg alloys have always been related to the precipitation of the Mg-rich β(Al₃Mg₂)-phase at the grain boundaries as the primary cause leading to these two types of corrosion attack [3,4,5,6,7]. The phenomenon is known as sensitization. The intergranular corrosion is widely associated with the selective dissolution of the β-phase (Al₃Mg₂), which is electrochemically more anodic than the surrounding bulk metal. The sensitization theory is based on studies made on modeled Al₃Mg₂ samples prepared in bulk form. These studies showed that the electrochemical open circuit potential (OCP) of these modeled phases is -1.15V_{SCE} approximately [8,9,10]. This value was taken as an indication of the electrochemical reactivity of the β-phase and was used to support a selective dissolution-base mechanism for the intergranular corrosion and for the IGSCC [11]. In fact it has been reported that SCC occurs when the β-phase exists as discrete particles along the grain boundary indicating that there must be a mechanism by which cracks propagate between particles but, until now, there is not a clear answer to this problem. Other mechanisms have been proposed including hydrogen embrittlement, enhanced plasticity in Mg-depleted zones along grain boundaries, and boundary cracking due to hydrogen embrittlement enhanced by Mg segregation [12,13]. Despite these theories, there is still disagreement on a common mechanism for the intergranular corrosion process. Therefore, the present chapter has the generic goal of understanding the effect of Mg content in the Al-Mg alloys as a precursor for intergranular corrosion susceptibility. In addition, a model for the initiation and propagation of intergranular corrosion based on the electrochemical behaviour of magnesium and aluminium is introduced.
6.2 Experimental

It was found that sample preparation is the most crucial step when Mg enrichment at grain boundaries needs to be measured. This is due to the fact that Mg reacts very easily in the presence of humid or aqueous environments. This situation often brings as a consequence a false idea that Mg enrichment does not occur [3, 4, 14, 15, 16]. Therefore in this section, the author will introduce two techniques to measure and/or visualize Mg enrichment.

The chemical composition of the studied alloys (AA5754, AA5018 and AA5083) has been previously given in chapters 4 and 5. All samples were cut from three commercial wrought aluminium alloy sheets in tandem rolled conditions (hot rolled until finish). All samples were ground with a 600-grit SiC (silicon carbide) paper removing approximately 1.5mm from the surface. This particular sample preparation process permitted the elimination of the existing deformed oxide layer produced by the fabrication process, obtaining in this way a more representative aluminium oxide on all samples with no MgO enrichment before experimentation. The samples were mechanically polished down to 0.25µm. Immediately afterwards, they were ultrasound cleaned and air-dried. All metal samples were sensitized in an air-circulating furnace at temperatures of 100°C and 200°C (each one for periods of 5, 11 and 30 days) followed by an air-cooling process until the samples achieved room temperature. In order to ensure reproducibility, a set of quadruplicates for each alloy was prepared following exactly the same experimental conditions.

In order to assess the effects of sensitizing temperatures on the intergranular corrosion susceptibility of the alloys, the samples were first characterized by light optical microscopy. The sensitized polished samples were immersed in concentrated nitric acid (HNO₃) for a period of 3 hours at room temperature. Three hours of immersion were found to be enough to help delineating the affected grain boundaries without damaging excessively the polished metal surface. Nitric acid is frequently used in ASTM standards to evaluate intergranular corrosion susceptibility on non heat-treatable aluminium alloys. This usage is based on the fact that nitric acid preferentially attacks magnesium rich areas and Mg-rich precipitates.

A complementary analysis was carried out by field emission gun scanning electron microscopy (FEG-SEM JSM-6500F) coupled with an energy dispersive X-ray analyzer.
(EDS). Additionally, a Nanoscope III multimode atomic force microscope (AFM) with a silicon tip covered with a conductive layer of Pt-Ir was employed for Volta potential mapping of the surface. For some of the analysis, the surface of sensitized polished samples was additionally treated with an alkaline sodium hydroxide solution (2.5M NaOH).

In order to clarify the use of nitric acid (HNO\textsubscript{3}) and sodium hydroxide (NaOH) as chemical treatments to visualize Mg enrichment on grain boundaries, first it is necessary to introduce some important chemistry concepts regarding magnesium. Magnesium (Mg) is an alkaline earth metal. In general, alkaline earth metals are considered to be very reactive elements but not as reactive as the alkali metals (lithium, sodium, potassium, etc). Nevertheless, all these elements have the ability to lose their valence electrons to non-metals (\textsubscript{aq}H\textsubscript{2}O, chloride, oxygen, fluorine, etc.) to form ionic compounds. Magnesium reacts with water to form Mg(OH)\textsubscript{2(aq)} plus hydrogen bubbles as a sub-product. The rate of this reaction is highly dependent on temperature and on pH. In other words, the rate of magnesium dissolution will be rather slow at low temperatures (T<5\textdegree C), and it will gradually rise as temperature increases. Only in the presence of strong alkaline conditions, Mg will be able to form a stable Mg(OH)\textsubscript{2} solid phase. This precipitation layer will continue to build up on the metal surface until it becomes thick enough to protect the magnesium metal. When this situation is reached, all electrochemical activity comes to an end and passivity is achieved.

In the case of aluminium, a sodium hydroxide aqueous solution induces a rather fast dissolution of the metal. In contrast when aluminium interacts with nitric acid solution, the dissolution of aluminium occurs at a slower rate (much slower than magnesium dissolution). Consequently when the Al-Mg sample is immersed in nitric acid, the magnesium will be preferentially dissolve at a faster rate while aluminium dissolves at a very slower rate. In the case of immersion in sodium hydroxide, aluminium will be preferentially dissolved at a faster rate whereas magnesium is in the process of passivation. These effects are illustrated in Figure 6-1. SEM micrographs demonstrating the effects of these etching techniques are shown in Figure 6-2.
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Figure 6-1. Illustration of the effects that a) nitric acid and b) sodium hydroxide have on the Mg enriched areas, respectively.

Figure 6-2. Etching effects on grain boundaries of an Al-Mg alloy when using a) nitric acid and b) sodium hydroxide.

Nevertheless in order to achieve fast passivation, it is required to supersede the solubility limit of the hydroxide compound, i.e. Mg(OH)$_2$, in a short period of time. Therefore, we used a small volume of the alkaline solution to prevent dilution of the Mg$^{2+}$ ion concentration being formed by dissolution. In this small volume of the alkaline solution with high OH$^-$ concentration, precipitation of Mg(OH)$_2$ takes place rapidly. This step is crucial to visualize the enrich areas as well as the Mg-rich precipitates. Therefore, in order to rapidly reach the solubility limit for Mg(OH)$_2$, two factors are necessary: high OH$^-$ concentration (strong base) and a small volume of the alkaline solution. In the present research, the concentration and amount of alkaline solution used for etching the Al-Mg samples was 2ml (milliliters) of 2.5 to 3M (mole/liter) NaOH. The exposure time of the surface to the alkaline solution was 20 to 30 seconds, approximately.
In addition to the techniques previously mentioned, a Field Emission Scanning Auger Nanoprobe (physical electronics PHI-700) was also employed to determine the composition of the grain boundaries. This system provides elemental information of sample surfaces, submicron features and interfaces with a spatial resolution of less than 6 nanometers. The primary electron energy used for this analysis was set at 20 KeV and the beam current was set between 1nA to 10nA. The electron beam was programmed to scan an area of approximately $2\mu m \times 2\mu m$. This area contains enough information of the chemical composition of the grain boundary and surrounding areas. Low energy Auger lines ($L_{2,3}VV$) as well as high energy ($KL_2L_2$) Auger lines were used to determined the element concentration of the analyzed area.

Sample preparation of the Al-Mg alloys was found to be crucial for FEG-Auger analysis as well. The main problem encountered was to find a way to quantify the Mg enrichment without chemically etching the surface. As previously explained, chemical etching has the major disadvantage of modifying the composition of Mg-rich areas. Moreover, sample preparation by means of electro polishing (frequently used in TEM analysis), mechanical polishing, or by using the focus ion beam (FIB) was also found to affect the magnesium concentration on the grain boundaries indicating a nearly inexistent Mg enrichment. In fact throughout the scientific literature, it is possible to see that detecting and quantifying Mg enrichment seems to be a difficult target to achieve. In fact, the author has found only three scientific publications where the researchers have managed to come up with some quantification of grain boundary enrichment [17,18,19]. Although the degree of enrichment varies for each publication, all of them have acknowledged the existence of Mg enrichment at grain boundaries.

The approach selected for sample preparation in FEG-Auger measurements was to sputter-etch the surface. The sputtering was performed using an argon ion beam with gun voltage of 3.5 kV and a gun current of 10 $\mu$A. The sputtered area was approximately $400\mu m \times 400\mu m$. SEM images were used to locate the potential grain boundary sites. After sputter cleaning most of the surface carbon was removed. However, no grain boundaries were visible (see Figure 6-3a and 6-3b). In an effort to confidently locate grain boundaries, the sample was sputter-etched to remove 320 nm of material. After the sputter-etching process, grain boundaries were visible in the SEM images (see Figure 6-3c and 6-3d). Three main areas
were identified by AES analysis: grain boundaries, transgranular surface and second phase particles. In this way, proper evaluation and quantification of grain boundary enrichment could be obtained.

![Figure 6-3](image)

Figure 6-3. Sample after sputter cleaning and removing 3nm from the surface (a and b) and after sputter-etching the surface (c and d) removing 320nm of material.

The data obtained was analyzed using the Phi Multipak data analysis program. This analysis involved a nine-point smooth (attenuation of noise in the signal) and a five-point differentiation. The peak-to peak differentiated signal amplitudes were used to calculate compositions. To establish appropriate sensitivity factors for the 700AES system, measurements were made for pure Mg and Al. This measurement resulted in relative sensitivity factors for Al 1396 peak/Mg 1188 peak of 1/1.33.

### 6.3 Results

#### 6.3.1 Intergranular attack on grain boundaries

After the sensitization treatment, some of the samples were mechanically polished using a neutral aqueous lubricant. The polishing procedure was done to help in the identification of second phase constituents and surface features before exposure to an aggressive medium. The
polished surface was characterized by SEM-EDX noticing that microscopic cracks were already formed on the surface of the alloy. These cracks appear to be related to a grain boundary dissolution process. Figures 6-4 through 6-6 show examples of grain boundary dissolution found for an AA5018 (3.5wt% Mg) sample after polishing the surface with a 0.25µm diamond paste plus a neutral aqueous lubricant.

Figure 6-4 illustrates the grain boundary attack of an AA5018 alloy sensitized at 200°C for 11 days after mechanical polishing. SEM micrographs and EDX analysis showed the presence of silicon-rich precipitates as well as some Al(Fe,Mn)Cr intermetallics. However, no Mg-precipitation could be detected near the grain boundaries. The intergranular dissolution
observed on the SEM micrographs seems to initiate far from the precipitates. It is also evident that the localized corrosion attack induced by the wet polishing process does not follow a continuous propagation path along the grain boundary, not even for a sensitized alloy. On the contrary, it seems that portion of the boundary has been dissolved while some intermediate parts appear to be intact. In addition, it can be seen that triple point grain boundary junctions appear to be much more susceptible to intergranular corrosion attack than other parts of the grain boundary. By performing EDX analysis on areas near the grain boundary (in the grain interior) and along the undissolve grain boundary, a sort of Mg enrichment is observed. A similar situation is found for the same alloy in different conditions: sensitized at 100°C (Figure 6-5) and as-received conditions (Figure 6-6). Both SEM micrographs show grain boundary corrosion attack and propagation along the grain boundary.

Figure 6-5. AA5018 (3.5%Mg) sensitized 100°C for 11 days

Figure 6-6. AA5018 (3.5% Mg) as received
Despite the limitations that EDX analysis technique has, the perceptible Mg enrichment on undissolved grain boundaries seem to be fairly reproducible. In fact, the number of EDX counts obtained for the enriched areas are much higher that the counts reported in the scientific literature [18,19]. Therefore, the data obtained by SEM-EDS analysis suggest that Mg enrichment can take place, and this enrichment could be linked to the susceptibility of the grain boundary to corrosion attack.

The SEM micrograph shown in Figure 6-7 displays some interesting features. It is possible to observe the presence of manganese (Mn) dispersoids (possibly Al₆Mn) plus what appears to be a sort of segregation within the solid solution. Mn dispersoids are usually found near the grain boundary area [20] and are characterized for having an oval-rhomboidal shape [20]. The presence of these dispersoids assists on the grain refinement during rolling. EDX composition analysis was performed on areas labelled as points 1 and 2 (Figure 6-7). By overlaying both EDX spectra, small magnesium enrichment can once again be observed. It is important to notice that the difference in Mg concentration detected on the EDS spectra is fairly small and values should be taken with caution. However, it is important to point out that the small differences in Mg concentration are reproducible but they cannot be taken as conclusive. Nevertheless, these results indicate that sensitization definitively induces changes on the corrosion susceptibility of the grain boundary.

Figure 6-7. AA5018 (3.5% Mg) sensitized at 200°C for 11 days.
6.3.2 Intergranular corrosion susceptibility as a function of sensitizing temperature

As mentioned in previous chapters, Mg additions to the alloy greater than 3.5 wt% increase the susceptibility of the alloy to intergranular corrosion attack, whereas lower Mg concentrations improve the corrosion resistance of the alloy. This susceptibility has been associated with what has been described as continuous precipitation of $\beta$-phase ($\text{Al}_3\text{Mg}_2$) along the grain boundary. Figures 6-8, 6-9 and 6-10 show the effects of different sensitizing temperatures on Al-Mg alloys with varying Mg concentrations.

Optical microscopy analysis was performed on an AA5754 polished sample with low-Mg content (2.7%) sensitized at 100°C and 200°C, and later compared to a reference-unsensitized sample. In order to visualize the effects of sensitizing temperatures, the samples were immersed in nitric acid ($\text{HNO}_3$) for a period of 3 hours. As previously mentioned, nitric acid tends to preferentially attack Mg-rich areas and Mg-rich precipitates. Consequently, these areas or precipitates will be dissolved. In Figures 6-8a and 6-8b, it is possible to observe that the corrosion attack is generally distributed all over the surface and only the precipitates are delineated due to the creation of microgalvanic cells with the aluminium matrix. Grain boundaries are not visible suggesting the absence of $\beta$-phase precipitation or Mg enrichment on these areas. In contrast, when the same sample with low Mg content is subjected to a sensitizing temperature of 200°C, the surface morphology of the alloy suffers some modifications (Figure 6-8c). Coarsening of cathodic precipitates takes place, producing additional areas where localized corrosion attack can initiate. In addition, it is possible to observe small-corroded lines possibly indicating the initiation of intergranular attack. However, the presence of these lines on the surface is sporadic and it is difficult to verify if these lines are related to a grain boundary. Nonetheless, these results indicate that a corrosion resistant alloy with low magnesium content starts to be susceptible to localized corrosion after being exposed continuously to 200°C.
Figure 6-8. Surface features of AA5754 (2.7wt%Mg) sample immersed in nitric acid for 3 hours in a) as received conditions and after being sensitized b) at 100°C and c) 200°C for 11 days prior to immersion.

Figure 6-9 shows the effect that sensitizing temperatures have on an AA5018 alloy. This alloy is considered to be in the border of corrosion resistance and susceptibility. In Figure 6-9a and b, it can be observed that the corrosion attack is once again generally distributed all over the surface and only the precipitates are delineated due to the creation of microgalvanic cells. However, Figure 6-9b shows a high concentration of localized attack in the form of pitting probably caused by the presence of fine cathodic precipitates. Clearly these fine particles were induced by the 100°C treatment. Some of the localized corrosion attack seems to be randomly distributed throughout the surface and some appears to be more concentrated at a particular location. Nonetheless, grain boundaries are still not visible suggesting the absence of β-phase precipitation or Mg enrichment on these areas. When the alloy is sensitized at 200°C (Figure 6-9c), changes in the surface morphology are much more evident. This time, delineation of fine lines can be observed. These lines appear to be continuous suggesting grain boundary dissolution due to the presence of Mg-rich precipitates or possibly Mg enrichment. Once again, a 200°C sensitizing temperature causes the major changes observed.

Figure 6-9. Surface features of AA5018 (3.5wt%Mg) sample immersed in nitric acid for 3 hours in a) as received conditions and after being sensitized b) at 100°C and c) 200°C for 11 days prior to immersion.
Figure 6-10 displays the effects that sensitization induces on an AA5083 alloy with higher Mg content (4.5wt% Mg). In Figure 6-10a, it is possible to see that the fabrication process has already induced precipitation on the grain boundary area. The precipitate distribution is more localized to a specific region rather than a more random distribution. It is evident from Figure 6-10a that delineation of the grain boundaries is not entirely well defined. Some grain boundaries are more visible than others perhaps due to their specific crystallographic structure and, hence different degree of precipitation. In other words, some grain boundaries allow easier Mg diffusion than others and consequently precipitation should be easier on one type of grain boundaries than others. This situation could determine which grain boundaries are more susceptible to corrosion and which ones are more resistant.

If raising the temperature to 100°C increases the Mg mobility, then it will be easier to observe a well defined grain boundary delineation over the entire surface. Figure 6-10b displays the surface features of the alloy sensitized at 100°C for 11 days. It can be observed that the corrosion attack is concentrated more on the grain boundaries and less on the grain interiors. It is also evident that the grain boundary lines are much better delineated indicating that corrosion is more evenly spread along the boundary. As temperature increases to 200°C, the corrosion attack shows to occur on a wider area of the grain boundary. The intergranular attack delineates a thicker boundary line suggesting that either the precipitates on this area have coarsened or a wider area has been enriched with magnesium. In addition, grain interiors show localized corrosion attack in the form of pitting, probably induced by the presence of fine precipitates. Immediately, it is possible to compare the low Mg and high Mg content samples and see that the grain boundary dissolution is different and the extension of
the attack is larger in samples with high Mg concentration. Another important difference is
that for the low Mg alloy the depth of the corrosion attack seems to be limited to small areas
than for the alloy with higher Mg content. Additionally, the temperature needed to provoke
intergranular corrosion susceptibility on AA5083 is much lower than for AA5754 and
AA5018 alloys.

6.3.3 Intergranular corrosion susceptibility as a function of sensitizing time
at a fixed temperature

Figure 6-11 shows the overall effect that 200°C sensitizing temperature has on the
microstructure of the aluminium alloy for prolonged periods of time. As mentioned before,
the alloys were immersed in concentrated nitric acid (HNO₃) for 3 hours to visualize the areas
with Mg-rich precipitation as well as possible Mg enrichment.

For the alloy AA5754 with low Mg content, the prolonged exposures to high temperatures
(200°C) provoke some interesting microstructural changes on the alloy. During the first 24
hours, pit-like attack caused by fine precipitates dominates most of the surface features. After
5 days of sensitization, the pits seem to become larger and more rounded pits. Consequently,
the localized attack seems to be more pronounced. The major change on the surface comes
after 11 days of sensitization. It is possible to observe larger and more rounded pitting attack
and these pits appear to be aligned following a specific pattern. In addition, some of the pits
outside this line have disappeared or decreased in size. After 30 days of exposure, the surface
shows thick and well-defined lines of localized corrosion attack. These lines follow a specific
patter that resembles a triple point grain boundary. In addition, larger pits decorate the
surface as well. These pits appear to be fairly deep.

Figure 6-11 also shows the effects that prolonged exposures to a sensitizing temperature of
200°C induce on the microstructure of an AA5018 alloy. The first 24 hours of exposure seem
to induce pit-like corrosion attack caused by fine precipitates. This effect appears to be as
comparable as when the alloy is exposed to 100°C for 11 days. Locations of those pits are
randomly distributed but few areas show higher concentration. No grain boundary attack is
visible. After 5 days of sensitization, delineation of grain boundary lines starts to appear.
However, these lines seem to be discontinuous and located in limited areas of the surface.
Also, pit-like attack is visible. After 11 days of exposure, a similar situation seems to
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continue but, this time, the localized corrosion at the grain boundaries appears to be thinner and more in a step-wise form. In addition, the number of pits shows to increase. After 30 days, more lines are formed due to localized corrosion attack. These corrosion attack lines appear to be thicker but still discontinuous.

Figure 6-11. Effects of 200°C sensitizing temperature as a function of time on commercial Al-Mg alloys with varying Mg content.
In the case of AA5083 with higher Mg content (Figure 6-11) shows the sensitizing effects are more dramatic. The alloy, in the as received condition, shows already precipitation on grain boundaries. As mentioned before, the grain boundary lines are discontinuous indicating that precipitation does not occur on all grain boundaries. After 24 hours of exposure to 200°C, the alloys shows similar surface features to the as-received conditions. However, the grain boundary attack shows to be much better defined. In other words, there is a higher degree of corrosion attack. This situation is much more evident after 5 days of sensitization. It is possible to observe that parts of the grain boundary are more heavily attacked displaying clearly the step-wise morphology of the intergranular corrosion. Moreover, pitting corrosion attack appears on the grain interiors. After 11 days, the grain boundaries are now well-defined indicating a strong corrosion attack on this area. In this case, the intergranular corrosion attack becomes visibly deeper. After 30 days of sensitization, the grain boundary attack is wider and much deeper covering the most of the surface.

From these results, it is evident that Mg concentration has an effect on the degree of susceptibility to corrosion attack. Low Mg content alloys show to be more resistant to intergranular attack while alloys with higher Mg content show to be highly susceptible. This susceptibility also depends on the temperature and length of the exposure. Published
literature indicates that SCC frequently occurs when the Mg-rich \( \beta \)-phase exists as discrete particles along the grain boundary [21,22] and with increasing magnesium concentration in the alloy and increasing aging time, the \( \beta \)-phase particle spacing decreases.

### 6.3.4 Visualization of magnesium enrichment at grain boundaries as a function of sensitizing temperature

Visualization of grain boundaries in Al-Mg alloys is achieved by using a sodium hydroxide (NaOH) solution. As previously mentioned, an alkaline etching solution (in particular NaOH) helps to passivate areas enriched with Mg while dissolving the aluminium matrix. Combining NaOH concentration, etching time and volume used, it is possible to control the amount of material dissolved inducing a smoother topography as well as revealing some interesting surface features. For instance, Figure 6-12 displays the delineation of Mg-rich areas along the grain boundary line as well as Mg-rich precipitates. It is important to notice that there is a clear distinction between the enriched grain boundaries and Mg-rich precipitates. Mg-rich precipitates show a much more brilliant white colour and display a very specific shape. The visibility of the grain boundary lines depends on the degree of Mg enrichment. More enrichment means a brighter white colour line, and vice versa. Precipitates, which have little or no Mg at all, display a gray to dark colour.

![Figure 6-12. Visualization of grain boundaries lines after passivation of the Mg-rich areas with NaOH on an AA5083 aluminium alloy sensitized at 100°C for 7 days.](image-url)
In an effort to corroborate the existence of Mg-rich lines, two major approaches were taken. The first approach was to use EDX analysis on these areas. The second option was to use an indirect approach based on the chemical characteristics of Mg and its compounds. The first approach proved to be unsuccessful mainly due to two reasons: lateral resolution of the EDX beam and the lack of discrimination between the bulk and the grain boundary composition.

The second approach proved to be much more successful. As previously stated, this approach was based on the chemical characteristics of the Mg-rich areas. Magnesium is a more electrochemically active element and, therefore, it shows a more anodic behaviour compared to the aluminium matrix. In addition, this potential difference should be directly dependent on the amount of magnesium present. Mg-rich precipitates possess higher Mg concentration per unit area than any Mg enrichment existing on a grain boundary. Therefore, Mg-rich precipitates should display a more anodic behaviour than enriched grain boundaries. In contrast, precipitates without Mg such as Fe-rich or Mn-rich particles should display a more cathodic (noble) behaviour than the aluminium matrix.

AFM Volta potential mapping was employed to verify Mg rich areas. Figure 6-13 shows the topography and the Volta potential mapping obtained by atomic force microscope (AFM) in the Kelvin probe (KP) mode. The Volta potential mapping obtained (Figure 6-13b) clearly shows that the grain boundary lines display an anodic behaviour. Mg-rich precipitates show also anodic behaviour but the magnitude is higher (more anodic) than the magnitude observed for the grain boundary. This situation is visible by the intensity of the dark colour on the Volta potential mapping. Cathodic particles observed on the topography map (Figure 6-13a) are clearly identified on the Volta potential map indicated as white particles. Unfortunately, a quantification of the Volta potential difference between the aluminium matrix and the grain boundary was impossible to obtain. There was a limitation on the spatial resolution of the AFM equipment used for these measurements and, consequently, an accurate value was impossible to achieve. Nonetheless, AFM Volta potential mapping allowed verification of the existence of Mg-rich grain boundaries corroborating their anodic nature.
Figure 6-13. SKP-AFM micrographs displaying a) topographic features such as grain boundaries and precipitates, and b) Volta potential mapping of the same area. Dark colours are assigned to anodic areas whereas bright white colours are assigned to cathodic regions.

Alkaline etching has proven to be a useful technique to observe magnesium enrichment at grain boundaries. This technique was employed to monitor the effects that sensitizing temperatures have on the Mg enrichment at grain boundaries. Figure 6-14 shows a low-Mg content alloy (AA5754) after being etched with NaOH. From this SEM micrograph is
possible to see large intermetallics as well as fine nano-particles decorating the surface. As expected on a low-Mg content alloy, grain boundary precipitation is rarely present. Only few grain boundaries have rod-like precipitates of less than 1µm in length. Also around the grain boundary area, it appears almost to be precipitate-free zone. The tonality of delineated lines also indicates that the Mg content inside the grain boundary is low. As sensitizing temperature increases to 100°C (Figure 6-15), a larger amount of precipitation is observed inside the grain. However around the grain boundary area, the number of precipitates has slightly increased. The boundary lines continue to be weakly delineated suggesting that the Mg enrichment at these areas remains unchanged. It is important to notice that Mg-rich precipitates at triple points were not found. At a sensitizing temperature of 200°C (Figure 6-16), the amount of precipitates in grain interiors and near the grain boundary area has increased. In contrast, only a handful of precipitates are found inside the grain boundary line (mainly Al₃Mg₂ precipitates). In addition for this sensitizing temperature, Mg-rich precipitates are formed at triple point junctions. Precipitates at triple point are not unusual since these triple points are characterized by having a spacious area where high concentration of Mg atoms can gather and form Mg-particles.

Figure 6-14. AA5754 (2.7%Mg) in as received conditions
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Figure 6-15. AA5754 (2.7%Mg) sensitized at 100°C for 7 days

Figure 6-16. AA5754 (2.7%Mg) sensitized at 200°C for 7 days

When the Mg content in the alloy is increased, it is possible to observe an increment in precipitation along the grain boundary as well as Mg enrichment. Figure 6-17 displays the surface features of a high-Mg content alloy (AA5083) in the as received condition after being etched with NaOH. From this SEM micrograph (Figure 6-17), it is evident that the number and size of precipitates along the grain boundaries have increased. However, these precipitates are still forming a non-continuous network arrangement. It is also found that most precipitates are formed in the triple-point junctions. Additionally, it is possible to identify a kind of elongated-clusters (2 to 3μm) of Mg along the grain boundary. These elongated clusters of magnesium seem to attach to other existing boundary precipitates.
For a sensitizing temperature of 100°C (Figure 6-18), the number of precipitates and the number of elongated magnesium clusters has increased. Some grain boundary precipitates seem to attract more magnesium to them. In other words, it seems like the elongated magnesium clusters are attracted to the precipitates probably to further nucleate increasing subsequently the particle’s size. This additional supply of Mg atoms accumulates along the grain boundary area ready to attach to an existing particle when possible. Therefore, the surface under these conditions has Mg-rich precipitate plus areas of Mg enrichment. The formation of these Mg-rich clusters along the grain boundary becomes much more evident when the alloy is sensitized at 200°C. At this temperature, the grain boundary lines are much better defined. It is evident that the Mg-rich clusters start to cover more area along the grain boundary forming an almost continuous network. In all cases, it is possible to see that precipitates in grain boundaries are most of the time connected by a thin line of Mg enrichment existing in the grain boundary as well. At this moment it is difficult to quantify the amount of Mg enrichment exiting on this area. As mentioned before, higher the magnesium concentration is, the more electrochemically active this area will be. Consequently, finding a technique that can accurately measure the concentration of magnesium on the grain boundary, near the grain boundary and far from the grain boundary (grain interior) becomes of great importance. This concentration profile could help to understand the mechanism of propagation of intergranular attack.

Figure 6-17. AA5083 (4.5% Mg) in as received conditions
6.3.5 Quantification of magnesium enrichment at the grain boundary by means of field-emission Auger

In order to confirm the existence of Mg enrichment in the grain boundary region, field emission Auger (FE-Auger) surface analysis was performed. The analysis was carried out at Physical Electronics-USA in Chanhassen, Minnesota. Certainly, the Phi (Φ) 700 Field Emission Scanning Auger Nanoprobe with its high spatial resolution is the appropriate technique to be used for this job. Normal Auger with a microprobe produces spectra that are influenced by both precipitates and segregated solute (see Chapter 4) and, hence, making difficult the discrimination of these regions. FE-Auger can clearly make that distinction.
Due to the limited access to the technique and time constraints, the analysis was restricted to only one AA5018 sample treated at 200°C for 11 days. This sample was selected based on the fact that its Mg bulk content lies between what is considered to be corrosion resistant and corrosion susceptible. As mentioned before, the process for Mg quantification at grain boundaries involved several challenges. One of the most important problems encountered was to find a way to detect and measure the enrichment without actually altering the magnesium concentration on the area. Consequently, any type of surface chemical treatment was immediately ruled out. Mechanical polishing of the surface only improved, until a certain degree, the topographical features of the surface but it did not allow the visualization of grain boundaries as it can be seen in Figure 6-20.

![Figure 6-20. a) Optical micrograph of the polished metal surface and b) Φ-SEM micrograph of the area indicated by the square box on a). The sample used is an AA5018 alloy sensitized at 200°C for 11 days.](image)

As a first approach, an area of 10µm² was scanned to check for the Mg bulk concentration. This first measurement gives an average Mg content of 3.8 atomic percent (at%). It is important to mention that this value includes the possible contribution of existing Mg-rich precipitates. Further SEM analysis at a higher magnification confirms the lack of distinction of the grain boundary region as it can be seen in Figure 6-21. However, it is possible to identify the presence of a large number of small precipitates randomly distributed on the metal surface. Composition Auger analysis performed on point 2 indicated in the SEM micrograph of Figure 6-21 shows that these fine precipitates are Si-rich particles. In fact, by etching the sample with nitric acid it is possible to reveal the Si-rich fine precipitates (Figure 134).
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6-22). Evidently they seem to be distributed all over the surface as well as responsible for the pitting attack observed on the metal surface.

Figure 6-21. Auger spectra obtained at the point indicated by point 1 and 2 on the Φ-SEM micrograph. The Mg bulk content was obtained in an area of 10µm² equivalent to an area shown on the SEM micrograph.

Figure 6-22. SEM micrographs illustrating the formation of Si-rich particles on the surface of sensitized AA5018 aluminium alloy. The surface was etched with nitric acid for 3 hours.
Figure 6-23 shows the Auger element mapping of the surface shown in the SEM micrograph of Figure 6-21. The element mapping does not reveal any Mg enrichment on the area or the presence of any Mg-rich precipitate. The series of results obtained at this point seem to suggest that Mg enrichment actually does not occur. However, they also demonstrate the importance of the sample preparation process for finding and measuring Mg enrichment at grain boundaries.

Figure 6-23. Auger element mapping for a sensitized AA5018 alloy sample. The scanned area was set to 10µm² similar to the area shown in Figure 21.

Figure 6-24 displays the surface after the sputter-etch process revealing grain boundaries and precipitates existing on the area. Sputter-etching the surface clearly permits to have major control of the surface details without modifying or erasing information due to chemical etching. In addition, Figure 6-24 also shows the Auger element mapping for this area. The Auger element mapping indicates the existence of Mn-rich particles near the grain boundary line, (Mg,Si) precipitates, and a big area of Mg-enrichment. Mn-rich particles (dispersoids) similar to the one shown in Figure 6-7 are known to have a composition that can be classified in the group of Al₆MnCr particles [20]. These types of precipitates are often difficult to find in the early stages of formation since they are often small within few nanometers beneath the surface layer. It is important to point out that there is a clear distinction between Mg-rich precipitates and Mg enrichment. The Mg element map shows a region of high Mg accumulation in a small area plus a large distribution of Mg belonging to a grain boundary with a width of 150 to 200nm, approximately. Comparing the Mg map with the Si map, it is possible to identify that the Si concentration matches the Mg concentration on a very small area suggesting the early formation of a (Mg, Si) precipitate, probably an Mg₃Si.
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Figure 6-24. Φ-SEM micrographs and Auger element mapping of the grain boundary area of a sensitized AA5018 aluminium alloy.

The details observed in the element mapping demonstrate the magnificent resolution of the FE-Auger, clearly displaying areas with high Mg concentration (i.e. grain boundaries) and Mg rich precipitates.

In terms of detecting Mg concentration gradients that indicate Mg enrichment on the grain boundary area, FE-Auger has proven to be a valuable tool. Figures 6-25 show Auger spectra obtained in the several points of the grain boundary area quantifying the element composition of this region. These points correspond to areas on the grain boundary line (points 1 and 4),
precipitates at and near the grain boundary (points 2 and 3), and far from the grain boundary line (point 5), approximately 900 to 1000nm away from the boundary.

Figure 6-25. Auger spectra taken at points shown in the Φ-SEM micrograph indicating the element concentration found at the grain boundary region.

From the Auger spectra shown in Figure 6-25, the composition of point 1 indicates 8.29 at% of Mg suggesting that Mg tend to accumulate close to some precipitates. This effect was also shown to occur when the sample was etched with NaOH, (see in Figures 6-2b, 6-17, 6-18 and 6-19). This result suggests that clustering of Mg atoms to subsequently form a precipitate can
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occur. Also, the existence of Mn-rich dispersoids close to the grain boundaries as shown in Figure 6-7 is confirmed by FE-Auger analysis. Auger spectra (Figure 6-25) taken at points 4 and 5 also illustrate the effects of Mg segregation to the grain boundary. The Mg concentration for point 4 is 14.37 at% at the grain boundary whereas far from this area (point 5) is 2.82at%. These results confirm the enrichment of Mg atoms that the grain boundary undergoes when the alloy is exposed to a sensitizing temperature. In addition, Cu is also found to be part of the grain boundary composition contributing with 5.06 at%. Cu is a minor alloying elements added to increase the strength of the alloy, which also has rather high mobility in the aluminium matrix. Therefore, it is not strange to have a small Cu enrichment in some grain boundaries since Cu enrichment has been reported for AA5083 alloy [18] and for AA2024 Al-Cu alloy [23]. The Cu enrichment under this condition was variable and was found not to occur on every grain boundary.

![Graph](attachment:image.png)

Figure 6-26. Mg concentration profile as a function of distance from the grain boundary and obtained by Auger line point scan. The analyzed area is indicated by a line depicted in the Φ-SEM micrograph. The dotted line (----) indicates the average Mg bulk content in the alloy.

Figure 6-26 displays the concentration profile obtained by measuring several points from the grain boundary towards the grain interior. The concentration profiles show a maximum Mg concentration at the grain boundary of 14.3 at%. This concentration decreases as we move away from the surface. The minimum Mg concentration measured was approximately 2 at% 700nm away from the grain boundary. After this point, the concentration starts to increase to values near the average Mg bulk content (3.8 at%). This result indicates that the supply of Mg comes from areas in the vicinity of the grain boundary, reaching a maximum concentration in the grain boundary line and a minimum outside the grain boundary (600 to 800 nm away). It is clear that Mg segregation can occur probably as a favoured equilibrium
process at sensitizing temperatures (as low as 70°C) which result in localized compositional increments at grain boundaries and these compositional increments can make the boundaries highly reactive.

6.4 Discussion

There are numerous observations linking the β-phase (Al₃Mg₂) constituents with the susceptibility to intergranular corrosion in Al-Mg alloys. The susceptibility is associated with increased grain boundary precipitation of the β-phase, with the greatest susceptibility associated with what has been described as continuous precipitation of β-phase particles along the grain boundary. However, Jones et al [18] demonstrated that SCC occurs when the β-phase exits as a discrete network rather than as a continuous network along the grain boundary. This situation, clearly suggests that it exists an additional mechanism by which cracks propagate between particles. Consequently, the initiation and propagation of the intergranular attack is found to be a more complicated process. Based on the experimental data obtained and the chemical characteristics of Mg plus some key information found in the literature, the author proposes a possible mechanism for the intergranular corrosion process in Al-Mg alloys.

The intergranular corrosion process in Al-Mg alloys may be related to the chemistry existing at the grain boundaries. The extent of the grain boundary role in the intergranular corrosion process may well be dependent on its specific density in the material, its crystallographic texture (distribution of grain misorientations and grain boundary plane orientations) and/or its chemical composition [24]. Changes on the grain boundary crystallography or chemical composition can result in modification of the intrinsic structure and properties of boundary [25]. Segregated atoms to the boundary can change the energy of a grain boundary [26]. Consequently, segregation of Mg to the grain boundary can become an important factor in the intergranular corrosion process.

However, it is possible to give an alternative explanation to the effect of Mg segregation to the grain boundary. Since Mg atoms are substantially larger (12%) than aluminium atoms, the segregation is largely controlled by size effects. Large atoms will tend to go to the expanded regions (i.e. grain boundaries, near precipitates, dislocations and surfaces) while
small atoms tend to move to the compressed regions. When Mg atoms escape to the grain boundary regions, the strain energy due to misfit in the bulk is much alleviated. This situation indicates that Mg segregation could be spontaneous. Mg atoms closer to the surface will immediately segregate to the surface while atoms closer to the grain boundaries will go to the grain boundaries. In addition, atoms closer to a dislocation will tend to go to the dislocation site and will remain there to later nucleate and grow into a precipitate. Mg-rich precipitates will also be formed at grain boundaries along with the formation of clusters of solute free atoms. Another factor that influences the movement of Mg atoms can be seen in the activation energy for Mg in aluminium ($Q_{Al-bulk}^{Mg} = 151 kJ/mol$, $Q_{Al-bulk}^{Al} = 175 kJ/mol$, for Mg in Al and Al in Al respectively). These activation energies show that Mg in the Al-bulk metal is more mobile than Al atoms. This situation mainly reflects the relative ease at which Mg atoms can move through the lattice. The rate at which Mg atoms diffuse along different boundaries cannot be the same but it will depend on the structure of the individual boundary. In other words, it is not expected that Mg enrichment, as well as formation of precipitates, occurs in every single grain boundary at the same time, but rather it is the result of the influence of a heat treatment process that helps Mg atoms to move faster and occupy all the free space available. This situation is evident for the alloy AA5083, shown in Figure 10. At room temperature, in the as-received condition, it is possible to see intergranular attack but this attack does not occur in all grain boundaries. However when the temperature is increased, the corrosion attack appears to be in every single grain boundary. Therefore, the reposition of solute atoms in the metal is greatly enhanced under the influence of a thermal gradient as low as 70°C, and the degree of Mg segregation and its impact on the corrosion resistance of the material will be determined by the length of exposure to this thermal treatment.

As it can be seen in Figures 6-8 through 6-11, this enrichment effect is dependent on the Mg bulk content (a.k.a. the Mg source or supplier). On one hand, alloys with high Mg content will concentrate more Mg in the grain boundary area inducing the formation of magnesium-rich precipitates. On the other hand, alloys with low Mg content will have less Mg in the grain boundaries (almost all Mg is in solid solution- there is no excess-) and consequently less formation of precipitates. Once again if the alloy is subjected to higher temperatures for prolonged times, Mg will have enough energy to overcome the activation barrier of the bulk to move and find a place where it can fit better. This effect is illustrated in Figures 6-14.
through 19. Most precipitates are formed in triple-point junctions because these areas are places where high concentration of Mg atoms can gather and form particles. Despite this non-continuous formation of precipitates, they are connected with a Mg-rich line along the grain boundary as it can be seen in Figures 6-14 through 6-19 as well. Movement of Mg atoms from the bulk to the surface is much more evident than the movement of magnesium atoms from the bulk to the grain boundary. The main reason for this difference is the space available on the surface is much greater than the existing space in the grain boundaries.

Magnesium accumulated in the grain boundary leads to a preferential dissolution of this area. Consequently, the chemical composition of the grain boundary will be modified going from a primarily Mg-rich area to a mainly Al-rich area due to the creation of a microgalvanic cell effect. If in the grain boundary there is enough precipitation, then precipitates will enhance the corrosion process increasing the rate of dissolution. One important point that should be addressed is the fact that the degree of enrichment is different for each grain boundary. In other words, the grain boundary’s characteristics (high-angle, low-angle, twin-boundaries, etc) determine the amount of Mg accumulated as well as the number of precipitates present in the grain boundary. In this way, magnesium can be labeled as the main factor triggering and subsequently inducing the propagation of intergranular corrosion in Al-Mg alloys.

In terms of the intergranular corrosion process, the chemical characteristics of Mg become very important. As previously mentioned, Magnesium (Mg) is located in the group of alkaline earth metals. Alkaline earth metals are considered to be very reactive elements but not as reactive as alkali metals (lithium, sodium, potassium, etc). Alkaline and alkali earth metals share a common characteristic: a strong oxygen affinity to form oxides by means of ionic bonding. These oxides are very unstable in the presence of aqueous environments producing a basic solution when dissolved in water plus hydrogen evolution as a sub-product:

Anodic partial reaction  \[ Mg \rightarrow Mg^{2+} + 2e \]

Cathodic partial reaction  \[ 2H_2O + 2e \rightarrow H_2 + 2OH^- , \]

and subsequent magnesium hydroxide formation given by
As mentioned in Chapter 4, Mg(OH)$_2$ could be a stable solid phase only under strong alkaline conditions, otherwise it will dissociate into the electrolyte. When this phase is dissolved, the OH$^-$ species will contribute to the pH increase of the solution (see Chapter 4). However, this increment on the solution’s pH will never be enough to induce passivation of the Mg enriched areas. Consequently, any Mg enrichment or precipitation will be dissolved in the presence of humidity or wet environments. Even if the Mg-enriched areas could form MgH$_2$ (magnesium hydride), this compound is highly unstable in wet conditions and chemically reacts to form hydrogen. Scully et al. [27] have experimentally found that lithium and magnesium as alloying addition in aluminium alloys increase the solubility of hydrogen in aluminium because of their chemical affinity for hydrogen. Therefore, the mechanism proposed is based on the electrochemistry of the $\beta$-phase, the Mg enrichment on grain boundaries both in contact with the aluminium matrix and the hydrogen uptake in aluminium.

In order to have a path for a crack to propagate, a necessary condition is the existence of a composition difference between the inside of the grain and the grain boundary. If an enrichment of the most reactive elements is higher than the composition of the grain interiors, dissolution of the reactive solute element will occur followed by slower dissolution of the aluminium grain boundary. Even though literature shows that Mg segregation decreases the grain boundary strength thus leading to an increase in grain boundary embrittlement [28], the author believes that Mg plus hydrogen segregation results in grain boundary embrittlement. In fact, hydrogen should embrittle the grain boundary more seriously than Mg at the same segregation concentration. Therefore, when the Al-Mg alloy is exposed to the electrolyte, the $\beta$-phase precipitates will immediately start to react. These precipitates should have higher potential difference with the aluminium matrix since they concentrate a larger amount of Mg atoms. Dissolution of these phases can be moderately fast involving hydrogen evolution. Following the $\beta$-phase reaction is the reaction of the grain boundaries enriched with magnesium. These areas concentrate less Mg per unit area than the $\beta$-phase particles. Consequently, the Mg at the grain boundaries reacts to produce hydrogen coupled with the magnesium dissolution. Hydrogen continues to diffuse into the grain boundary provoking embrittlement. In other words, magnesium segregation to grain boundaries should promote
hydrogen-induced crack growth, while a heavy presence of Mg-rich precipitates at grain boundaries can only speed up the process.

### 6.5 Conclusions

Mg plays an important role in the corrosion characteristics of Al-Mg alloy. Grain boundary enrichment of magnesium (or other alloying elements) is an important factor in the intergranular corrosion mechanism. Enrichment of one or more alloying elements plus the presence of precipitates in the grain boundary provides the conditions for the creation of microgalvanic cells, which induce selective dissolution of the grain boundary. It was found that the amount of enrichment strongly depends on the bulk concentration in the aluminium matrix, on the sensitizing temperature and time of exposure as well as mobility of the alloying atoms in the bulk. These results indicate that a corrosion resistant alloy with low magnesium content can be susceptible to intergranular corrosion after being exposed continuously for prolonged periods of time. On the other hand, alloys with high Mg content are susceptible to intergranular corrosion attack almost immediately. Figure 6-27 illustrates this situation.

![Figure 6-27. Intergranular corrosion susceptibility of Al-Mg alloys for a constant temperature](image)

A mechanism for intergranular corrosion is also proposed. This mechanism is based on the combination of three main factors: magnesium-rich precipitates at grain boundaries, magnesium enrichments at grain boundaries, and hydrogen diffusion into the grain boundaries. It was observed that precipitates at grain boundaries are most of the time connected by a thin line of Mg enrichment existing also in the grain boundary. When the Al-Mg alloy is exposed to a wet or humid environment, the \( \beta \)-phase precipitates will immediately
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start to react. Dissolution of these magnesium-rich phases occurs fairly fast, involving in the reaction hydrogen evolution. Following the \( \beta \)-phase reaction is the reaction of the grain boundaries enriched with magnesium also involving hydrogen evolution during the magnesium dissolution. Thus in this way, hydrogen continues to diffuse into the grain boundary provoking embrittlement. Therefore, magnesium segregation to grain boundaries should promote hydrogen-induced crack growth while a heavy presence of Mg-rich precipitates at grain boundaries greatly speed up this process.

6.6 References


9 E.H. Dix, W.A. Anderson and M.B. Shumaker, Corrosion, 15, 2, p. 19 (1959)


Summary

An investigation concerning the effects of magnesium on the intergranular corrosion susceptibility of AA5XXX alloys was carried out. As previously mentioned, magnesium plays an important role on the 5XXX alloy series as a major alloying element. Magnesium provides substantial strength to the aluminium metal by solid solution strengthening. Consequently, there is a strong incentive to make alloys with higher magnesium concentrations in order to achieve high strengths. The 5xxx series spans a wide range of magnesium contents designed for a variety of applications. In addition, information often found in metals handbooks suggests that the addition of magnesium in aluminium alloys improves the corrosion resistance of the metal. However, experience has shown that this corrosion resistance strongly depends on the Mg bulk content in the alloy, the surrounding temperature as well as the surrounding media in which these alloys are going to be employed.

In the present work, magnesium is found to be highly mobile in the bulk metal as well as in the aluminium oxide. This mobility is also found to be dependent on the temperature and bulk magnesium concentration. Interestingly, the corrosion susceptibility of the AA5XXX series appears to be directly related to the magnesium mobility as well. Magnesium surface enrichment and grain boundary precipitation/enrichment are consequence of the high mobility of the magnesium atoms.

Based on the theories proposed by Macdonald and Habazaki (chapter 3), it is found that magnesium is the most favoured alloying element in the aluminium metal that actively contributes to the formation and composition of the oxide layer. Nevertheless, the extent of this contribution strongly depends on the magnesium content of the alloy and the applied temperature (chapter 4). Auger composition-depth profiles performed on alloys with different Mg contents indicate that when the bulk magnesium concentration is high, the Mg enrichment on the oxide layer becomes stronger. This situation brings as a consequence the formation of thicker oxide layers. In contrast when the Mg content in the alloy is low, the magnesium enrichment on the oxide layer becomes smaller as well as its contribution to the oxide layer
thickness. The magnesium enrichment is found to be always located on the outer part of the oxide layer. However, this magnesium distribution in the oxide layer is dependent on the time of exposure to the sensitizing temperature. For instance at room temperature, the enrichment rate will be extremely slow. Hence in order to obtain a higher Mg concentration in the oxide layer, it is necessary to wait long periods of time. In contrast at 200°C, the enrichment obtained in the oxide layer can reach up to 40wt% in just 11 days. At even higher temperatures, the percent of enrichment increases in shorter periods of time.

Some publications suggest that the magnesium enrichment of the oxide layer enhances the dissolution rate of the AA5XXX alloys. However, results obtained (chapter 4) indicate that enrichment on the oxide layer has little or no effect on the corrosion rate of the alloy. This effect can be seen on the open circuit potential curves obtained for the sensitized and unsensitized alloys (chapter 4). It is observed that during the first two hours of immersion of the metal into a sodium chloride (NaCl) solution, the open circuit potential of the alloy is pushed to more active (negative) potentials as a function of degree of enrichment. Nonetheless, this electrochemically active behaviour of the alloyed surface becomes gradually passive due to the selective dissolution of the magnesium-rich areas. The transients observed on the open circuit potential curves are caused by the magnesium dissolution. This selective dissolution also causes a small increase on the surface pH. The magnitude of the pH increase observed is directly proportional to the degree of surface enrichment. After approximately 5 hours of continuous immersion, the electrochemical behaviour of the surface gradually becomes dominated by the aluminium oxide layer reaction. Therefore, a magnesium enriched oxide layer has a rather limited effect on the overall electrochemical behaviour of the alloyed surface.

Prolonged exposure to moderated temperatures such as 100°C and 200°C induce changes in the properties of the 5XXX aluminium alloys (Chapter 5). These changes can be summarized as follows:

- Low Mg content alloys display a stronger response to micro-hardness changes induced by temperature and time of exposure. On the other hand, stronger electrical conductivity variations induced by temperature are observed on alloys with higher Mg content.
• Changes on electrical conductivity and micro-hardness obtained as a function of sensitizing temperature suggest that the Mg content in the alloy decreases.
• Prolonged exposures to moderated temperatures affect mainly precipitates containing magnesium and silicon. It is observed that long periods of exposure increase the number and size of Si-rich and (Mg,Si) phases.
• Al(Mn,Fe,Cr) or Al(Mn,Fe,Cr)Si particles dominate the type of precipitates found in commercial Al-Mg alloys. In second place are Si-rich and (Mg,Si) precipitates (except Mg$_2$Si which are rarely found in the alloy).
• Si-rich precipitates are found to be present near the grain boundaries as well as Mn dispersoids.

The enrichment on grain boundaries is reflected in the form of heavy precipitation of Mg-rich particles and/or heavy concentration of Mg solute-free atoms. It is important to keep in mind that alloys with Mg content below 3.5wt% are considered having Mg nearly or completely in solid solution and, consequently, the formation of Mg-rich particles (often $\beta$-Al$_3$Mg$_2$ phase) appears to be randomly distributed over the metal surface. In contrast, when the bulk Mg content exceeds 3.5wt%, the solid solution of the alloy is considered to be supersaturated. As a result, the formation of Mg-rich precipitates is found to be mainly concentrated on grain boundaries.

Precipitates such as Al(Mn,Cr,Fe) and Al(Mn,Fe) are found to be between 5µm to 20µm in length and their location, in most occasions, is on the path of the grain boundaries. Almost all of these particles are located at grain boundaries and sometimes at triple points. Despite of their location, these particles are found to not contribute to the intergranular corrosion process. At most, they contribute to mild localized corrosion in the form of particle induced pitting. Moderate sensitizing temperatures and prolonged exposures do not appear to inflict any effect on Al(Mn,Cr,Fe) and Al(Mn,Fe) phases.

Al(Mg,Si), Mg$_2$Si as well as Si-rich phases are also found at or near grain boundaries. Their size varies between $\frac{1}{2}$ to 5µm. Elemental mappings and line scans help to visualize the effects that extended periods at sensitizing temperatures affect these particles. The results obtained (chapter 5) indicate that prolonged exposures to sensitizing temperatures affect
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mainly the Mg content in the Mg-rich phases and, consequently, their size. In addition, prolonged exposures favoured the formation of fine Si-rich particles on the metal surface.

Detection and quantification of grain boundary magnesium enrichment was obtained by Field-Emission Auger analysis. Magnesium is found to be a more electrochemically active element and, therefore, more anodic compared to the aluminium matrix. Mg-rich precipitates possess higher Mg concentration per unit area than any Mg enrichment existing on a grain boundary. Consequently, magnesium-rich precipitates are found to display a more anodic behaviour than enriched grain boundaries. In contrast, precipitates without Mg such as Fe-rich or Mn-rich particles are found to display a more cathodic (noble) behaviour than the aluminium matrix. It is also observed that precipitates in grain boundaries are most of the time connected with a thin line of Mg enrichment existing in the grain boundary.

On the present work, a mechanism for intergranular corrosion is proposed. This mechanism is based on the combination of three main factors: magnesium-rich precipitates at grain boundaries, magnesium enrichments at grain boundaries, and hydrogen diffusion into the grain boundaries. It was observed that precipitates at grain boundaries are most of the time connected by a thin line of Mg enrichment existing also in the grain boundary. When the Al-Mg alloy is exposed to a wet or humid environment, the $\beta$-phase precipitates will immediately start to react. Dissolution of these magnesium-rich phases occurs fairly fast, involving in the reaction hydrogen evolution. Parallel to $\beta$-phase reaction is the reaction of magnesium enriched grain boundaries involving once again hydrogen evolution. Thus in this way, hydrogen can continue to diffuse into the grain boundary provoking embrittlement. Magnesium accumulated in the grain boundary leads to a preferential dissolution of this area. If at the grain boundary there is enough precipitation then precipitates will enhance the corrosion process increasing the rate of dissolution. Consequently, magnesium enrichment at grain boundaries provides the conditions to promote hydrogen-induced crack growth, while a heavy presence of Mg-rich precipitates at grain boundaries help to speed up this process.
Samenvatting

Er werd onderzoek uitgevoerd naar de effecten van magnesium op de intergranulaire corrosievatbaarheid van AA5XXX-legeringen. Zoals eerder vermeld speelt magnesium een belangrijke rol op de 5XXX-legeringsreeks als hoofdelement in de legering. Magnesium levert substantiële stevigheid aan het aluminiummetaal door het versterken van de vaste oplossing. Dientengevolge is er een sterke drang legeringen met een hogere concentratie aan magnesium te maken om deze hoge stevigheid te verkrijgen. De 5XXX-reeks omvat een breed scala aan magnesiumgehalten ontworpen voor een verscheidenheid aan toepassingen. Bovendien brengt informatie die vaak in handboeken voor metalen gevonden wordt, te berde dat de toevoeging van magnesium in aluminiumlegeringen de corrosieweerstand van het metaal verbetert. Ervaring heeft echter uitgewezen dat deze corrosieweerstand sterk afhangt van het magnesiumhalte van Mg in de legering, de omgevingstemperatuur en de omgevingsstoffen waarin deze legeringen zullen worden ingezet.

In het onderhavige werk werd ontdekt dat magnesium zeer mobil is in het massametaal alsmede in het aluminiumoxide. Van de mobiliteit werd eveneens ontdekt dat deze afhankelijk is van de temperatuur en massa van de magnesiumconcentratie. Interessant daarbij is dat de corrosievatbaarheid van de AA5XXX-reeks ook direct gerelateerd blijkt te zijn aan de magnesiummobiliteit. Oppervlakteverrijking en korrelgrensafscheiding door magnesium zijn gevolgen van de hoge mobiliteit van de magnesiumatomen.

Gebaseerd op de theorieën die zijn opgesteld door Macdonald en Habazaki (hoofdstuk 3) werd ontdekt dat magnesium het meest favoriete legeringselement in het aluminiummetaal is, welk element actief bijdraagt aan de vorming en samenstelling van de oxidelaag. Desondanks hangt de mate van deze bijdrage sterk af van het magnesiumgehalte van de legering en de toegepaste temperatuur (hoofdstuk 4). Samenstelling-diepteprofielen volgens Auger-analyse uitgevoerd op legeringen met verschillende Mg-gehalten, geven aan dat wanneer de massaconcentratie van het magnesium hoog is, de Mg-verrijking op de oxidelaag sterker
Samenvatting

wordt. Deze situatie heeft tot gevolg dat er dikkere oxidelagen worden gevormd. Daar staat tegenover dat wanneer het Mg-gehalte in de legering laag is, de magnesiumverrijking op de oxidelag en zijn bijdrage aan de dikte van de oxidelag ook kleiner wordt. Er werd ontdekt dat de magnesiumverrijking altijd aan het buitengedeelte van de oxidelag is gelocaliseerd. Deze verspreiding van het magnesium in de oxidelag is echter afhankelijk van de tijd dat het is blootgesteld aan de sensibilisatietemperatuur. Op kamertemperatuur is de verrijkingssnelheid bijvoorbeeld extreem laag. Om daarom een hogere Mg-concentratie in de oxidelag te verkrijgen, moet er langdurig gewacht worden. Daarentegen op een temperatuur van 200 °C kan de verrijking in de oxidelag al binnen 11 dagen oplopen tot 40wt%. Op nog hogere temperaturen loopt het percentage verrijking in nog kortere tijd op.

In sommige publicaties wordt voorgesteld dat de magnesiumverrijking van de oxidelag de ontbindingssnelheid van de AA5XXX-lergeringen verbetert. Uit de verkregen resultaten (hoofdstuk 4) blijkt echter dat verrijking op de oxidelag weinig tot geen effect op de corrosiesnelheid van de legering heeft. Dit effect kan gezien worden in de krommen van het nullastvermogen, verkregen voor de gesensibiliseerde en niet-gesensibiliseerde legeringen (hoofdstuk 4). Er werd waargenomen dat tijdens de eerste twee uur van onderdompeling van het metaal in een natriumchloride-oplossing (NaCl) het nullastvermogen van de legering naar de actievere (negatieve) potentialen wordt geduwd als functie van de graad van verrijking. Dit elektrochemisch actieve gedrag van het legeringsoppervlak wordt echter geleidelijk passief vanwege de selectieve ontbinding van de gebieden die rijk zijn aan magnesium. De overgangen die in de krommen van het nullastvermogen werden waargenomen, worden veroorzaakt door de magnesiumontbinding. Deze selectieve ontbinding veroorzaakt ook een geringe toename van het oppervlakte-pH. De omvang van de pH-toename die werd waargenomen, is direct evenredig aan de graad van oppervlakteverrijking. Na ongeveer 5 uur van continue onderdompeling wordt het elektrochemisch gedrag van het oppervlak geleidelijk gedomineerd door de reactie in de aluminiumoxidelag. Daarom heeft een met magnesium verrijkte oxidelag een redelijk beperkt effect op het gehele elektrochemisch gedrag van het legeringsoppervlak.
Langere blootstellingstijd aan matige temperaturen zoals 100°C en 200°C leidt tot veranderingen in de verhoudingen van de 5XXX-aluminiumlegeringen (hoofdstuk 5). Deze veranderingen kunnen als volgt worden samengevat:

- Legeringen met een laag Mg-gehalte vertonen een sterkere reactie op veranderingen in microhardheid, veroorzaakt door de temperatuur en blootstellingstijd. Aan de andere kant werden grotere variaties in de elektrische geleidbaarheid in legeringen met een hoger Mg-gehalte waargenomen, veroorzaakt door de temperatuur.
- Veranderingen in de elektrische geleidbaarheid en microhardheid verkregen als een functie van de sensibilisatietemperatuur duidt erop dat het Mg-gehalte in de legering vermindert.
- Langere blootstellingstijd aan matige temperaturen heeft hoofdzakelijk effect op afzettingen met magnesium en silicone. Er werd waargenomen dat lange blootstellingsperioden het aantal en de omvang van Si-rijke en (Mg, Si)-fasen vergroot.
- Al(Mn,Fe,Cr) of Al(Mn,Fe,Cr)Si-deeltjes domineren het type afscheiding dat gevonden wordt in de handel verkrijgbare Al-Mg-legeringen. Op de tweede plaats komen Si-rijke en (Mg, Si)-afzettingen (behalve Mg$_2$Si, dat zelden in de legering wordt gevonden).
- Si-rijke neerslag wordt gevonden bij de korrelgrenzen en bij de Mn-dispersoïden.

De verrijking op korrelgrenzen wordt gereflecteerd in de vorm van hevige neerslag van Mg-rijke deeltjes en/of hevige concentratie van Mg-oplossingsvrije atomen. Het is belangrijk te onthouden dat in legeringen met een Mg-gehalte onder de 3.5wt%, er van het Mg wordt verwacht bijna of volledig in vaste oplossing te zijn en dat dientengevolge de vorming van Mg-rijke deeltjes (vaak β-Al$_3$Mg$_2$-fase) willekeurig verdeeld over het metaaloppervlak voorkomt. Daarentegen wordt de vaste oplossing van de legering als oververzadigd gezien, wanneer het massagehalte van Mg boven de 3.5wt% uitstijgt. Het resultaat is dat de vorming van Mg-rijke afzettingen hoofdzakelijk op korrelgrenzen wordt gevonden.

Afzettingen zoals Al(Mn,Cr,Fe) en Al(Mn,Fe) zijn meestal tussen de 5µm en 20µm lang en de neerslagplaats is in de meeste gevallen op het pad van de korrelgrenzen te vinden. Bijna al deze deeltjes zijn gevonden bij korrelgrenzen en soms op tripelpunten. Ondanks hun locatie is
er ontdekt dat deze deeltjes niet bijdragen aan het intergranulaire corrosieproces. Ze dragen ten hoogste bij aan een matige plaatselijke corrosie in de vorm van een door deeltjes opgewekte puntroestvorming. Matige sensibilisatietemperaturen en langere blootstelling schijnen geen effect te hebben op de Al(Mn,Cr, Fe)- en Al(Mn,Fe)-fasen.

Al(Mg, Si), Mg₃Si en Si-rijke fasen worden ook op of nabij korrelgrenzen gevonden. Hun omvang varieert tussen de ½ tot 5µm. Elementaire mapping- en lijncans helpen mee aan de visualisatie van de effecten die de langere perioden van sensibilisatietemperaturen op deze deeltjes hebben. De verkregen resultaten (hoofdstuk 5) geven aan dat langere blootstelling op sensibilisatietemperaturen hoofdzakelijk effect hebben op het Mg-gehalte in de Mg-rijke fasen en dus op hun omvang. Bovendien bevordert de langere blootstelling de vorming van fijne Si-rijke deeltjes op het metaaloppervlak.

De detectie en kwalificatie van magnesiumverrijking op korrelgrenzen werd verkregen door Auger-analyse van veldemissies. Er werd ontdekt dat magnesium als element electrochemisch actiever is en daarom meer anodisch is vergeleken met de aluminiummatrix. Mg-rijke afzettingen bevatten hogere concentraties Mg per eenheidgebied dan een Mg-verrijking die op een korrelgrens bestaat. Daarom werd er ontdekt dat magnesiumrijke afzettingen een meer anodisch gedrag vertoonden dan de verrijkte korrelgrenzen. Daar staat tegenover dat afzettingen zonder Mg zoals Fe-rijke of Mn-rijke deeltjes een meer cathodisch (edeler) gedrag vertoonden dan de aluminiummatrix. Er werd eveneens waargenomen dat afzettingen in korrelgrenzen voor het merendeel verbonden zijn met een dunne lijn van Mg-verrijking die op de korrelgrens bestaat.

Voor het onderhavige werk werd een mechanisme voor intergranulaire corrosie voorgesteld. Dit mechanisme is gebaseerd op de combinatie van drie hoofdfactoren: magnesiumrijke afzettingen op korrelgrenzen, magnesiumverrijking op korrelgrenzen en waterstofdiffusie in de korrelgrenzen. Er werd waargenomen dat afzettingen op korrelgrenzen voor het merendeel verbonden zijn met een dunne lijn van Mg-verrijking die eveneens op de korrelgrens bestaat. Wanneer de Al-Mg-legering wordt blootgesteld aan een natte of vochtige omgeving, beginnen de β-fase-afzettingen direct te reageren. Ontbinding van deze magnesiumrijke fasen verschijnt erg snel, waarbij waterstofontwikkeling in de reactie wordt betrokken. Parallel lopend aan de
β-fase-reactie is de reactie van magnesiumverrijkte korrelgrenzen die opnieuw waterstofontwikkeling erbij betrekken. Op deze manier kan waterstof dus blijven diffuseren in de korrelgrens en broosheid veroorzaken. Magnesium dat in de korrelgrens ophoopt, leidt tot een voorkeursontbinding van dit gebied. Als er op de korrelgrens genoeg neerslag is, dan verhogen de afzettingen het corrosieproces waardoor de ontbindingsgraad toeneemt. Dientengevolge levert de magnesiumverrijking op korrelgrenzen de condities voor waterstofopgewekte kerfgroei, terwijl een grote aanwezigheid van Mg-rijke afzettingen op korrelgrenzen dit proces helpt versnellen.
Acknowledgements

Since the thesis work is never the effort of only one person, I would like to express my gratitude to my two promotors, Prof. dr J.H.W. de Wit and Prof. dr. ir. H. Terryn for their guidance, support and motivation. The author also acknowledges Corus for providing the material used in this thesis. I would like to thank the people of the department of metallurgy, electrochemistry and material science of VUB for their help, for their excellent conversation and for making me feel always welcome. I would like to especially acknowledge Oscar Steenhaut for his invaluable contribution to this work and his dedication on always obtaining good data for me. Oscar, thank you very much! I greatly appreciate it! I also would like to thank Dennis Paul from Physical Electronics (PHI) in the United States for his help on the FEG-Auger analysis, so crucial for this thesis. In addition, thank you to Isabelle Vandendael for accepting the dangerous mission of taking care of my samples while travelling to the US and for her constant communication during the experiments.

Four years of new experiences on a foreign country always leave nice memories. That is why I would like to thank the corrosion group members (past and present) for the pleasant collaboration over the past years: Paola, Francesco, Mae, Jeroen, Saskia, Wouter, Xiaolong, Chris, Zeeshan, Premendra, Natalia Frederic, Bart, (one of the most brilliant technicians in the Netherlands) and Gerrit Bakker. In particular, I like to thank Mae Looi for her invaluable assistance and contribution to this thesis. Thanks Mae! Thanks to my “officemates” (Chris, Prem, and Xiaolong) for great moments, fun memories and great conversations. Definitively, Our office was the best office in the entire building (also, the most visited!). Thanks to all the persons that, in one way or the other, have made such a nice impact in my life (the Spanish, Italian, French, Turkish communities plus the few Mexicans, Canadians, and Venezuelans of Delft). Great parties!

Thank you to my family for their irreplaceable support. Gracias, Papá, Mamá por apoyarme siempre, en todo momento. Finally, thanks Elo for pushing me so much to finish my thesis… It worked!
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