Corrosion evaluation of Bare and Anodized Magnesium Alloys in Physiological Media

Ana Isabel Martins Tiago Fernandes

in fulfillment with thesis requirement for the degree of

Master of Science in Chemical Engineering

Examinig Committee
Chair: Prof. Dr. João Carlos Moura Bordado (IST)
Advisors: Prof. Dr. João Carlos Salvador Fernandes (IST)
Dr. Lech Kwiatkowski (IMP)
Reviewer: Prof. Dr. Fátima Montemor (IST)

November 2011
Corrosion evaluation of Bare and Anodized Magnesium Alloys in Physiological Media

Ana Isabel Martins Tiago Fernandes

in fulfillment with thesis requirement for the degree of

Master of Science in Chemical Engineering

Examining Committee

Chair: Prof. Dr. João Carlos Moura Bordado (IST)
Advisors: Prof. Dr. João Carlos Salvador Fernandes (IST)
Dr. Lech Kwiatkowski (IMP)
Reviewer: Prof. Dr. Fátima Montemor (IST)

November 2011
Acknowledgements

Firstly I would like to express my deepest gratitude to Prof. João Salvador Fernandes, my supervisor at Instituto Superior Técnico, for giving me the opportunity to work on this project. I want to thank not only for his knowledge and insightful support but also for his willingness during the course of this work.

I am also thankful to Dr. Lech Kwiatkowski, my supervisor at Institute of Precision Mechanics, for all his orientation, availability and helpful advices during my stay in Warsaw.

I acknowledge the funding from FCT/ERA-MNT-0012009 and my colleague and co-supervisors that work in the same project.

I want to express my sincere gratitude to Dr. Piotr Tomassi, for his kindness and endless support while teaching me.

My work wouldn’t have been completed without the important help of dr. Anna Zych who helped me with the EIS measurements and Eng. Alicja Bałkowiec for the SEM measurements.

I want to extend my greatest appreciation for those who contribute to my very pleasant experience all through my stay in Poland. Dziękuję!

I also want to thank Prof. Fátima Montemor for her helpful suggestions and technical discussions. Her contribution with the XPS analysis greatly enriched this work.

My work was definitely improved with the help of all my colleagues and Professors at the Grupo de Estudos de Corrosão e Efeitos Ambientais of IST. A special thank to Dasha who aided me with the use of scanning electron microscopy.

I am short of words for the immeasurable emotional support of my family, especially of my parents, brother and sister. To all my friends who helped me in one way or another.

Finally, I dedicate this work to Francisco, once again he was my inspiration.
“It doesn't matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn't agree with experiment, it's wrong.”

Richard Feynman
Abstract

Biocompatible metallic materials represent the state of art for medical implants. After decades trying to develop strategies to minimize the corrosion of metallic biomaterials, there is actually an increasing interest in using an intentional corrodible alloy in a number of critical medical devices.

A number of recent works have emphasized the use of magnesium alloys as a new class of bioresorbable materials for orthopaedic implants. They combine multiple interesting and useful properties such as biocompatibility and osteoactive properties, low density, elastic modulus and compressive yield strength close to natural bones and the elimination of surgery for implant retrieval.

However, some key issues still lack of a precise study and improvement. Problems such as in vivo reabsorption being too rapid, too localized and unpredictable; and the fact that Mg corrosion produces hydrogen gas which may accumulate adjacent to the implant in the body still need to be overcome.

This study consists in the characterization of two different magnesium alloys (WE54 and AZ31) regarding their electrochemical behaviour. Particular attention was focused on the effect of specific ions present on physiological media and on the effect of temperature. Good agreement was observed between the results obtained from electrochemical techniques and those from SEM and XPS examinations. Mg(OH)$_2$ and calcium phosphate compounds are the main resultant products from the corrosion of Mg alloys which, despite the little protectiveness against degradation, confer excellent biocompatibility properties to the material.

In order to delay the initial corrosion rate plasma electrolytic oxidation was used to grow protective coatings in AZ31. Silicate- and phosphate-based electrolytes have been used and a substantial improvement of corrosion resistance was observed.

Keywords: Magnesium, Biodegradable implants, AZ31, WE54, Hank’s solution, Electrochemical impedance spectroscopy, Plasma electrolytic oxidation
Resumo

Os materiais metálicos biocompatíveis desempenham um papel essencial no campo das aplicações biomédicas, tendo recentemente vindo a assistir-se a um interesse crescente na utilização de ligas de magnésio para implantes ortopédicos.

Com efeito, estas ligas apresentam uma combinação única de propriedades, tais como uma boa biocompatibilidade, baixa densidade e ainda um módulo de Young e uma tensão de cedência semelhantes às do osso humano. No entanto, existem ainda alguns factores chave que podem limitar o uso destas ligas, nomeadamente o seu comportamento face à corrosão. Com efeito, a corrosão destas ligas coloca alguns problemas, como taxas de reabsorção “in vivo” demasiado elevadas ou ainda o facto de a corrosão ser acompanhada pela libertação de hidrogénio gasoso que se pode vir a acumular nos tecidos adjacentes ao implante. A resolução destes problemas exige assim um conhecimento aprofundado do comportamento electroquímico das ligas de magnésio em contacto com meios fisiológicos.

O objectivo deste trabalho, que se enquadra num projecto de investigação mais vasto visando a modificação de superfície de ligas de magnésio para aplicações biomédicas, consiste no estudo do comportamento face à corrosão e na caracterização de superfícies de duas ligas de magnésio em contacto com meios fisiológicos. Os resultados apresentados darão especial relevância ao efeito da temperatura e dos íons específicos presentes no meio. Observou-se uma boa concordância entre os resultados obtidos através de técnicas electroquímicas e análise de microscopia electrónica de varrimento e espectroscopia fotoeléctronica de raios-X. Mg(OH)₂ compostos de fosfato de cálcio são os principais produtos de corrosão das ligas de Mg em soluções fisiológicas que, apesar da baixa protecção contra a degradação, conferem excelentes propriedades de biocompatibilidade ao material.

A fim de retardar o processo de corrosão inicial, o método de oxidação por plasma electrolítico foi utilizada para proteger a superfície da liga AZ31. Foram utilizados electrólitos à base de silicatos e fosfatos tendo-se observado uma melhoria substanital da resistência à corrosão das amostras.

**Palavras-Chave:** Magnésio, Implantes biodegradáveis, AZ31, WE54, Solução de Hank, Espectroscopia de impedância electroquímica, Oxidação por plasma electrolítico
Contents

Acknowledgements.................................................................................................................................. 3
Abstract.................................................................................................................................................. 5
Resumo ................................................................................................................................................... 6
Contents.................................................................................................................................................. 7
List of Tables........................................................................................................................................... 9
List of Figures......................................................................................................................................... 10
List of Abbreviations and Symbols ....................................................................................................... 12

1. Introduction ....................................................................................................................................... 13
2. Literature Review ............................................................................................................................... 15
   2.1. Historical Background on Magnesium ....................................................................................... 15
   2.2. Magnesium as a biodegradable implant material ....................................................................... 16
       2.2.1. Short history of the use of magnesium as orthopaedic material ................................... 20
   2.3. Definition of Corrosion ............................................................................................................... 21
       2.3.1. Principles of Metallic Corrosion ......................................................................................... 22
           2.3.1.1. Electrochemical nature of corrosion ....................................................................... 22
           2.3.1.2. Measures and evaluation of corrosion ................................................................. 25
   2.4. Corrosion mechanisms of Mg and its alloys ............................................................................. 27
       2.4.1. Galvanic corrosion ............................................................................................................. 29
       2.4.2. Stress corrosion and stress corrosion cracking .............................................................. 30
   2.5. Progresses on surface modification of magnesium alloys ......................................................... 30
3. Materials and Methods ..................................................................................................................... 34
   3.1. Samples ....................................................................................................................................... 34
   3.2. Solutions ...................................................................................................................................... 34
   3.3. Experimental Conditions .......................................................................................................... 35
       3.3.1. Experimental Techniques ............................................................................................... 35
           3.3.1.1. Open Circuit Potential ............................................................................................ 35
           3.3.1.2. Electrochemical Impedance Spectroscopy ............................................................ 36
               3.3.1.2.1. Impedance Definition .................................................................................... 37
           3.3.1.3. Surface characterization ......................................................................................... 44
               3.3.1.3.1. Scanning Electron Microscopy .................................................................... 44
               3.3.1.3.1.1. X-Ray Photoelectron Spectroscopy ......................................................... 46
3.3.2. Comparison between the two media (NaCl and Hank’s solution) and the two alloys (WE54 and AZ31) ........................................................................................................... 47

3.3.2.1. Sample preparation and Electrochemical tests ........................................... 47

3.3.2.2. Analytical and Surface Characterization ...................................................... 48

3.3.3. Plasma Electrolytic Oxidation treatment ....................................................... 49

3.3.3.1. Surface preparation and pre-treatment ....................................................... 49

3.3.3.2. PEO treatment and characterization ......................................................... 50

5. Results .................................................................................................................. 52

5.1. Comparison between the two media (NaCl and Hank’s solution) and the two alloys (WE54 and AZ31) ........................................................................................................... 52

5.1.1. Open Circuit Potential Results ................................................................... 53

5.1.2. Electrochemical impedance Spectroscopy Results ...................................... 54

5.1.3. Ecompositional Analysis by X-Ray Photoelectron Spectroscopys ............... 58

5.1.4. Microscopic and Quantitative Analysis by Scanning Electron Microscopy ..... 60

5.2. PEO treatment .................................................................................................. 64

5.2.1. Characterization after PEO treatment ........................................................... 64

6. Conclusions and Future Work ............................................................................ 72

7. References .......................................................................................................... 75

Appendix ..................................................................................................................... 85
List of Tables

**Table 1** Physical and mechanical properties of current clinical biomaterials [10]..........................19
**Table 2** – The Electromotive Force Series (adapted from: [48]).............................................................24
**Table 4** Chemical Composition of the tested magnesium alloys..........................................................34
**Table 4** Ionic composition of Hank’s balanced salt solution, simulated body fluid (SBF) and blood plasma [77] ........................................................................................................................................35
**Table 5** Basic elements of an equivalent electrial circuit ........................................................................40
**Table 6** Chemical Composition of Electrolyte solutions used ..............................................................51
**Table 7** EDS results before immersion and after 24h in NaCl and Hank’s Solution ...............................62
**Table 8** General parameters and direct results obtained after PEO treatment .....................................65
List of Figures

Figure 1 First airplane nearly completely designed with magnesium – Northrop XP-56..........................16
Figure 2 Fluorescent images of cross-sections of degradable implants, (a) polymer and (b) magnesium rod.........................................................................................................................18
Figure 3 Biodegradable Mg-based stent developed by Biotronik Company [31] .................................19
Figure 4 Lambotte shows a supracondylar humerus fracture of a child (A), which was fixated using a magnesium nail (B). After several months the magnesium nail was totally corroded and the fracture was stable as presented in the two plane X-rays (C and D)..........................................................20
Figure 5 Schematic description of the determination of the corrosion rate for Mg from an experimental polarization curve (black solid line) using the Tafel slopes (red dashed line)..........26
Figure 6 Reactions between magnesium alloys and aqueous environment....................................................28
Figure 7 Pourbaix diagram of Mg showing the range of corrosion, passivation and immunity........28
Figure 8 Schematic description of a ceramic coating prepared by PEO process. In this particular example the layers of a MAGOXID® coating are shown (adapted from [78]).......................32
Figure 9 Schematic representation of the Nyquist and Bode plots for a resistor [83]..........................38
Figure 10 Nyquist and Bode plots for R (RC) circuit [80].................................................................40
Figure 11 Equivalent circuit for the interpretation of the impedance plots of Figure 10 .................41
Figure 12 Components of a Scanning Electron Microscope. Adapted from [88] ..............................45
Figure 13 Schematic representation of the elements in an electrochemical cell...............................48
Figure 14 Magnesium sample preparation for PEO treatment. An aluminium wire, correctly isolated was used to established the electrical connection ...................................................50
Figure 15 The two approaches followed during the PEO treatment: (a) Step and (b) pulse current programmes..............................................................................................................................50
Figure 16 OCP evolution AZ31 and WE54 alloys immersed for 45 minutes in NaCl (0.05 M) and Hank’s solution (Troom and 37°C).................................................................................53
Figure 17 Bode plots of WE54 and AZ31 alloys immersed in NaCl for 4, 12 and 24 hours ...............55
Figure 18 Bode plots of WE54 and AZ31 alloys immersed in Hank’s solution (pH 7.40) at (a) room temperature and (b) 37°C for 4, 12 and 24 hours .................................................................56
Figure 19 |Z| evolution with time for WE54 and AZ31 immersed in NaCl in the low frequency range (0.01 Hz).................................................................................................................................57
Figure 20 |Z| evolution with time for WE54 and AZ31 immersed in Hank’s solution at room T in the low frequency range (0.01 Hz).................................................................58
Figure 21 |Z| evolution with time for WE54 and AZ31 immersed in Hank’s solution at room T in the low frequency range (0.01 Hz). .................................................................58

Figure 22 XPS ionization spectra for a) Ca2p and b) P2p of WE54 immersed for 24h in Hank’s solution (XPS analysis performed by Dr. Fátima Montemor). .................................................................59

Figure 23 XPS ionization spectra for a) Ca2p and b) P2p of AZ31 immersed for 24h in Hank’s solution (XPS analysis performed by Dr. Fátima Montemor). .................................................................59

Figure 24 SEM images of (a) WE54 and (b) AZ31 alloys before immersion. ........................................60

Figure 25 SEM images of WE54 after immersion in 0.05 M NaCl at room temperature for (a) 1 and (b) 24h and in Hank’s solution at 37ºC for (c) 1 and (b) 24h, respectively..........................60

Figure 26 SEM images of AZ31 after immersion in 0.05 M NaCl at room temperature for (a) 1 and (b) 24h and in Hank’s solution at 37ºC for (c) 1 and (b) 24h, respectively..........................61

Figure 27 EDS analysis of AZ31 and WE54 in NaCl (Tamb) and Hank’s solution (37ºC) after 24h ...62

Figure 28 Bode plots of AZ31 treated samples in different electrolytes (M2, M3, M3 + M2, M2 + M6 and M6 + M2) after immersed in SBF for 5, 10 h and 1 day (EIS measurements by dr. Anna Zych)..........................................................................................................................................67

Figure 29 Bode plots of AZ31 treated samples in different electrolytes (M2, M3, M3 + M2, M2 + M6 and M6 + M2) after immersed in SBF for 2 days (EIS measurements by dr. Anna Zych)........68

Figure 30 Bode plots of AZ31 treated samples in M3 electrolyte after immersed for 5, 10h, 1, 2 and 3 days. The impedance values were kept constant. (EIS measurements by dr. Anna Zych)....68

Figure 31 SEM images of AZ31 after PEO treatment in M2 solution .................................................69

Figure 32 Chemical content along cross section of AZ31 after PEO treatment in M2 solution......69

Figure 33 SEM images of AZ31 after PEO treatment in M3 solution. .................................................70

Figure 34 Chemical content along cross section of AZ31 after PEO treatment in M3 solution......70

Figure 35 SEM images of AZ31 after 2-step PEO treatment in M3 and M2 solution.........................70

Figure 36 Chemical content along cross section of AZ31 after 2-step PEO treatment in M3 + M2 solution. ....................................................................................................................................................70

Figure 37 Chemical content along cross section of AZ31 after 2-step PEO treatment in M4 + M2 solution. ....................................................................................................................................................71

Figure 38 Chemical content along cross section of AZ31 after 2-step PEO treatment in M2 + M4 solution. ....................................................................................................................................................71

Figure 39 SEM images of AZ31 after 2-step PEO treatment in M4 and M2 solution.......................71

Figure 40 SEM images of AZ31 after 2-step PEO treatment in M2 and M4 solution.......................71
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSE</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant analyser energy</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>LEIS</td>
<td>Localized electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>PEO</td>
<td>Plasma electrolytic oxidation</td>
</tr>
<tr>
<td>RE</td>
<td>Rare earth</td>
</tr>
<tr>
<td>SBF</td>
<td>Simulated body fluid</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress corrosion cracking</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Saturated hydrogen electrode</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>$T_{room}$</td>
<td>Room temperature</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular Frequency</td>
</tr>
<tr>
<td>$V$</td>
<td>Potential</td>
</tr>
<tr>
<td>$I$</td>
<td>Electrical current</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Phase angle</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
</tr>
<tr>
<td>$L$</td>
<td>Inductance</td>
</tr>
<tr>
<td>$R_O$</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Double layer capacitance</td>
</tr>
</tbody>
</table>
1. Introduction

Every year millions of people suffer bone fractures as a result of disease or accident. In the years that follow, the increase of life expectancy in the industrialized countries is consequently leading to a higher number of fractures caused by age related illnesses such as osteoporosis [1].

Metallic materials represent a crucial group of biomaterials used in the repair or replacement of such diseased or damaged bone tissue [2]. Nevertheless these materials are not biodegradable in the human body conditions, possibly leading to long-term problems, which might result in a second surgery for implant recovery [3], which besides being inconvenient for the patient implies costs for the health systems.

In this sense, when it comes to orthopaedic applications, the major disadvantage of magnesium in industrial engineering applications (the weak resistance to corrosion) can turn into an advantage, with the Mg resultant corrosion products being non-toxic and naturally excreted via the kidneys.

As a potential degradable component, magnesium provides biocompatibility and also good mechanical properties [1, 3, 4]. Mg\(^{2+}\) is undoubtedly an important bivalent ion and a vital element involved in many metabolism and biological mechanisms [5, 6]. Studies relate its role to the formation of biological apatite, and its influence on bone osteoclasts and bone metabolism [7, 8, 27]. Compared to current implant materials, magnesium alloys have a lower elastic modulus (41-45 GPa which is close to that of natural bones (3-20 GPa)) [9] and higher yield strength, that provide to these alloys the potential for avoiding the “stress shield” caused by current metallic implants made of stainless steel or titanium alloys [7]. Furthermore, magnesium implants may in fact work as a stimulus for the re-growth of bone tissue as a result of specific functional roles, minimizing the inflammatory response [10, 11]. Consequently, magnesium and its alloys are extensively being studied and improved in order to enable their application as lightweight, degradable and load bearing orthopaedic implants, which would remain present in the body without losing their mechanical integrity over a period of 12–18 weeks while the damaged bone tissue is healing [10].

However, their use as implant is seriously limited due to their poor corrosion resistance in the physiological pH (7.4-7.6) – 10.5 to 210 mm per year for Mg with a purity of 99.9% [7] - thereby losing their mechanical integrity before the proper healing of the bone tissue is achieved and to the release hydrogen gas as a result of the corrosion processes, at rate that is excessively fast to be dealt with by the host tissue. Hence, a suitable degradation rate is determinant for the
promising future of Mg and its alloys as body implants [12]. Once finished the repair or healing of the injured bone tissue, the implant should be gradually dissolved or absorbed in the human body [10, 13].

A full understanding of the corrosion behaviour of magnesium in simulated body fluids is required in order to explore the possibility of employing magnesium alloys as biodegradable implants. Only with a sufficient knowledge of the corrosion mechanisms it will be possible to tailor the degradation rates according to the final application. Several studies [6, 14 - 16] have also shown that the corrosion behaviour of Mg alloys is strongly dependent on the alloying elements and their microstructure. The present work aims to compare the in vitro electrochemical degradation behaviour of WE54 alloy to that of the widely researched AZ31 alloy, aiming to reinforce the progress of biodegradable magnesium implants. Their corrosion behaviour was studied through the analysis of corrosion resistance variation with immersion time, using electrochemical impedance spectroscopy (EIS) tests and the surface morphology before and after immersion was analysed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The growth of anodic layers in the sparking zone (Plasma Electrolytic Oxidizing – PEO coatings) will also be developed and analysed. It is the goal of this study to examine the corrosion behaviour in simulated body fluid of coated samples prepared with different alkaline electrolyte solutions and with various oxide thicknesses. Corrosion resistance of these treated samples in solutions simulating the physiological environment will be evaluated by EIS and SEM, using standard corrosion tests.
2. Literature Review

2.1. Historical Background on Magnesium

Magnesium compounds such as hydroxides, sulphates and carbonates have been widely used and studied throughout history. With his name deriving from the ancient city of Magnesia in the Northern part of Greece, magnesium is found to be the 6th most abundant element, constituting 2% of the total mass of the Earth’s crust. Additionally, seawater contains 0.14% of magnesium, thus creating an almost endless reserve [17].

Nevertheless, it was not until 1755, when Joseph Black discovered that magnesia (MgO) was composed of a new element, that the notion of magnesium as a single chemical element emerged. The credit for first having isolated this element is usually attributed to Sir Humphrey Davy, who in 1808 documented that magnesium oxide (MgO), or magnesia, was the oxide of a newly discovered metal. He decomposed wet magnesium sulphate (MgSO₄) by electrolysis using a voltaic cell and a mercury cathode. Twenty years later the French scientist Antoine Alexander Brutus Bussy fused dehydrated magnesium chloride (MgCl₂) with metallic potassium at elevated temperatures to obtain metallic magnesium. The first production of pure metallic magnesium by electrolytic reduction from the molten magnesium chloride was accomplished in 1833 by Michael Faraday, the famous British scientist and former assistant of Sir Humphrey [18, 19]. Based on these experiments the German chemist Robert Wilhelm Bunsen constructed, in 1852, a small electrolytic cell to produce larger amounts of magnesium from molten anhydrous magnesium chloride [18].

The production of commercial magnesium began in 1886, in Germany, using a modification of Bunsen’s cell. In 1896, this process was jointly taken up by Chemische-Fabrik Griesheim-Elektron and Aluminium und Magnesium Fabrik as the sole significant supplier of magnesium metal in the world until 1914-1915 [20]. This fact was the reason why magnesium was called the “German metal” [19]. For several years, the world production of magnesium metal was used almost entirely in wire or powder form for photographic and pyrotechnical purposes and as a reducing agent in the production of aluminium [19]. These initial Mg products were presented at the world exhibition in London in 1862 [21].
By 1900, worldwide production had only reached approximately 10 tonnes per annum. The magnesium alloys were subjected to an initial development in parallel with other metal alloys. However, owing to some technical difficulties associated with the struggle in improving mechanical and corrosion properties along with profitable production of magnesium through alloy development, these early ventures were curtailed [17]. By 1915, yearly production had risen to only 250 tonnes. Then, several other countries began production, and the global annual production reached more than 3000 tonnes at the time of the First World War, falling again to 330 tonnes in 1920. The weight reduction achieved by using magnesium components was particularly interesting for the army and the rising aeronautic industry (Figure 1).

With the onset of the Second World War magnesium production reached a maximum of 228 000 tonnes per year in 1944, only to fall again in the late 1940s [17, 22].

![Figure 1](image_url) First airplane nearly completely designed with magnesium – Northrop XP-56. Reproduced from [23].

During the 1980s, the study and development of magnesium alloys with enhanced corrosion resistance, increased production to levels that reached and exceeded the Second World War ranks (360 000 tonnes in 1998) [22, 23]. Currently magnesium and its alloys are essentially applied in light-weight applications in the transport industry, aiming to achieve a substantial reduction in fuel consumptions and gas emissions, in accordance with the requirements for a more sustainable use of natural resources and controlled environmental impact [22].

### 2.2. Magnesium as a biodegradable implant material

Besides its applications in the transport industry, magnesium is also considered an interesting candidate for biodegradable implants because, apart from being physiologically compatible and biodegradable in the human body, it also stimulates bone formation [24, 25]. When it comes to orthopaedic applications, the major disadvantage of magnesium in industrial engineering
applications (the weak resistance to corrosion) can turn into an advantage. However, the high corrosion rate of Mg alloys must be accurately controlled either by selecting suitable alloying elements or by undergoing surface modifications on the magnesium parts.

Magnesium is a vital element involved in several metabolic and biological mechanisms [5, 8] and is mainly present in the bone, muscle and soft tissues; the adult body contains around 21-28 g of Mg (about 1 mole) [26]. Studies related its role in the formation of biological apatite, and its influence on bone osteoclasts and bone metabolism [7, 8, 27] working as a stimulus for the re-growth of bone-tissue, minimizing the inflammatory response. In fact, in a rat model, increased osteoclast activity and decreased bone density was observed during a magnesium reduction diet [28]. In an in vivo study followed by Witte et al. was observed that in relation to a polymeric degradable implant, more bone mass was formed around the Mg implant, as seen in Figure 2 [10, 11, 24, 25].

Although magnesium is needed in relatively big quantities in the human body, magnesium based implants should not corrode too quickly, particularly right after the implantation process, period when the implant requires sufficient strength while waiting for the tissue to be adequately healed. Moreover, the pH increase and the hydrogen gas released during the reaction of Mg (Eq. 1) in aqueous media might also be harmful to the tissue around the implant. The hydrogen gas produced either disappears along time or is removed by a perforation, which can be painful for the patient [24].

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad \text{Eq. 1}
\]

In general, the use of degradable implants avoids the need for a second operation for implant removal, which, besides being beneficial to the patient, saves money to the health system. This is particularly important for paediatric cases because the body is still changing and growing which thus requires the permanent implants to match the growth. Additionally, degradable implants also stimulate the damaged tissue as a result of a gradual load transfer from the implant to the tissue (see Figure 2) [24, 25]. The optimal degradation performance of a biodegradable orthopaedic implant must be controlled. It must be initially slow to ensure the total mechanical integrity of the tissue as well as biocompatibility by delaying the formation of degradation products. The length of this period depends on the respective use. After this stage the implant starts degrading over time while the load is being transferred to the bone until the tissue has healed and obtained its (full) strength. The currently available biodegradable polymers, such as polyglycolide and polydioxanone have been clinically used as surgical materials during the last decades; nevertheless they exhibit weak mechanical properties to be used as bone implants.
Figure 2 Fluorescent images of cross-sections of degradable implants, (a) polymer and (b) magnesium rod, respectively, performed 10 mm below the trochanter major in a guinea pig femur. Both specimens were harvested 18 weeks postoperatively. It can be seen that Mg stimulates bone formation. I indicates implant residual, P periosteal bone formation and E endosteal bone formation. Reproduced from [24].

Besides, when compared to current metallic implant materials, magnesium shows mechanical characteristics dimensionally comparable to those of natural bone (Table 1) [10]. Conventional metallic implants are too stiff. For instance, the elastic modulus (also known as Young’s modulus) of cobalt-chromium alloys ranges between 200 and 230 GPa while the corresponding value for natural bone varies between 3 and 20 GPa, the same occurring for implants made of stainless steel or titanium alloys [7]. This difference will therefore lead to the stress shielding (which emerges from the difference in stiffness/Young’s modulus between implant and bone) of the injured bone since it will deprive the bone of its normal stress compromising the whole healing process as well as the implant stability [1, 29]. Furthermore, in metallic permanent implants which are essentially passive in biological environments, the release of toxic debris due to wear corrosion may occur resulting in inflammation reactions [30].

For these reasons, a magnesium implant resuming all the advantages mentioned, which would remain in the body without losing its mechanical integrity over a period of 12–18 weeks while the fractured bone tissue heals [10] represents the state of art in biodegradable implant applications.


Table 1 Physical and mechanical properties of current clinical biomaterials [10]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g/cm(^3))</th>
<th>Elastic moduli (GPa)</th>
<th>Compression strength (MPa)</th>
<th>Toughness (MPam(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural bone</td>
<td>1.8 – 2.1</td>
<td>3 - 20</td>
<td>130 - 180</td>
<td>3 – 6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.74 – 2.0</td>
<td>41 – 45</td>
<td>65 – 100</td>
<td>15 – 40</td>
</tr>
<tr>
<td>Titanium Alloys</td>
<td>4.4 – 4.5</td>
<td>110 – 117</td>
<td>758 – 1117</td>
<td>55 – 115</td>
</tr>
<tr>
<td>Co-Cr Alloys</td>
<td>8.3 – 9.2</td>
<td>200 - 230</td>
<td>450 – 1000</td>
<td>-</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>7.9 – 8.1</td>
<td>189 – 205</td>
<td>170 – 310</td>
<td>50 – 200</td>
</tr>
<tr>
<td>Synthesized HA</td>
<td>3.1</td>
<td>73 – 117</td>
<td>600</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Currently, magnesium alloys find two main applications in biomaterials: biodegradable hard tissue repairing implant and biodegradable stents. Figure 3 exhibits a biodegradable stent developed by Biotronik Company in Germany [31]. This biodegradable stent mainly works in the coronary artery to inhibit the obstruction of a vessel (angiemphraxis) and vasoconstriction, which works for a period of 6 to 12 months.

Figure 3 Biodegradable Mg-based stent developed by Biotronik Company [31]
2.2.1. Short history of the use of magnesium as orthopaedic material

As a biodegradable implant, the use of magnesium dates back to the end of the 19th century with the physician Edward C. Huse stating that the corrosion of Mg was slower \textit{in vivo}. In 1878, he used some Mg ropes as ligatures to stop bleeding vessels of three patients. In 1892, Erwin Payr, an Austrian physician started his first experiments on Mg reabsorption and observed that the oxygen, the water content, the carbon dioxide, the blood salts and the chemical processes in cells were mainly responsible for the corrosion of Mg \textit{in vivo}. In 1906 Albin Lambotte used a pure Mg plate combined with gold coated steel screws as a degradable orthopaedic material for the fixation of a fractured tibia \cite{32}. However, the Mg plate corroded too quickly, and one day after the operation a large quantity of gas was observed under the skin. Due to the heavy pain, Lambotte removed the Mg plate at the end of 8 days \cite{32, 33}. With this shocking experience he understood that Mg dissolved due to the electrochemical reaction between the Mg plate and the steel screws \cite{21}. Regardless of this drawback he continued his clinical experiments. He successfully treated several supracondylar humerus fractures of children using Mg nails with a small implant extra-articularly (Figure 4). The evolved gas cavities disappeared after several weeks and were not a major concern in any clinical case \cite{32}.

\textbf{Figure 4} Lambotte shows a supracondylar humerus fracture of a child (A), which was fixated using a magnesium nail (B). After several months the magnesium nail was totally corroded and the fracture was stable as presented in the two plane X-rays (C and D). No infection or pain occurred. The child had a good clinical function of the elbow. Reproduced from \cite{21}. 
In 1913, Hey Groves investigated the use of Mg metal as an intramedullary peg and observed enhanced callus formation, but also fast degradation and fracture of the pegs. Thus, he suggested that magnesium was unsuitable to fix ordinary fractures, but appropriate for old un-united fractures [34].

Later, in 1934, Verbrugge (former Lambotte’s assistant) noticed, after some experiments using a Mg-8Al alloy, that a new callus formed and that Mg was completely absorbed, without showing any adverse reactions or toxicity. The degradation rate was slow and the evolved hydrogen didn’t cause any harm but just a temporary “sleepy” feeling [35, 36]. Similar findings were also achieved by McBride. He observed that screws were more resistant to corrosion than plates and stated that Mg was suitable in hard cortical bone, restricting the use of Mg in oblique or condylar fractures only to fractures where slight stress was placed on the implants [33].

Regardless of these auspicious outcomes, only little additional research was undertaken and it was not until the beginning of the current century that new investigations regarding this subject were re-taken, [24, 36]. Several Mg alloys were chosen for potential use as biodegradable implants, leading to many studies focused on the degradation behaviour in vitro [7, 39 - 44] and in vivo [24, 42, 43, 45]. Nevertheless, to date only few examples of Mg-based degradable implants are available in the market, as mentioned in the previous section.

Since the corrosion behaviour of magnesium is a key subject, with regard to biodegradable implants, this issue will be explained in detail in the next chapters.

2.3. Definition of Corrosion

Defining “corrosion” becomes particularly complicated since the term is constantly being extended. In literature one of the most accepted definitions found is: “Corrosion is the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment” [46]. This broad definition comprehends all types of materials such as: ceramics, polymers and natural materials.

However, as later shown by Shreir et al. [47], the definitions supported on the concept of degradation do not describe all the phenomena associated with corrosion, particularly those concerning corrosion of metals. An obvious example is the formation, in certain environments, of
an oxide layer in the surface of the metal, which in particular cases prevents or retards the metal degradation.

In corrosion science, metallic corrosion represents a critical subject, especially when in contact or exposed to aggressive media, such as moisture and aqueous environments. Therefore, in the next section we intend to give a clearer idea on the basic electrochemical concepts governing the metallic corrosion, as an introduction for a more meticulous analysis on the corrosion behaviour of magnesium and its alloys, upcoming in section 2.4.

2.3.1. Principles of Metallic Corrosion

What causes metals corrosion when in contact with an aqueous solution is simple to understand and is easily explained by the 2\textsuperscript{nd} Principle of Thermodynamics which, essentially, states that: “the matter tends towards a maximum state of disorder”. Therefore, since the atoms that constitute the metal are in relatively ordered state, surface atoms will tend to leave the crystal lattice, in order to reduce their chemical potential (or free energy) because the whole system tends towards a state of minimum energy (3\textsuperscript{rd} Principle of Thermodynamics) [48].

2.3.1.1. Electrochemical nature of Corrosion

Fundamentally, the corrosion of metals is the result of the electrochemical reactions (reactions in which the valence or oxidation state of a substance changes) taking place at the surface of the metal. An electrochemical reaction consists of four main steps: it involves an anodic process in which an atom is oxidized passing to the solution as a positive ion while its electrons with its inherent negative charge remain on the metal surface; it requires a cathodic reaction to consume the electrons released, reducing a species existent in the solution; this solution, the electrolyte, is required to carry the ions to and from the metallic surface and finally an electronic circuit capable of conducting the electrons from the anode to the cathode.

The mentioned electrochemical reactions are required to start at the same time for the corrosion process to arise spontaneously. The number of electrons consumed in the cathode (reduction) must equal the number of electrons produced in the anode (oxidation) which characterizes one of the basic principles in corrosion: oxidation and reduction events cannot occur separately.
The reactions that take place in solution can be separated as oxidation or reduction reactions, and can be described by their partial equation reactions as followed:

\[
\begin{align*}
\text{Me} & \rightarrow \text{Me}^{n+} + ne^- & \text{Eq. 2} \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 & \text{Eq. 3} \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} & \text{Eq. 4} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- & \text{Eq. 5} \\
\text{Me}^{n+} + e^- & \rightarrow \text{Me}^{n-1} & \text{Eq. 6} \\
\text{Me}^{n+} + ne^- & \rightarrow \text{Me} & \text{Eq. 7}
\end{align*}
\]

The anodic reaction (Eq. 2) represents the oxidation of a metal into its ion form; on the other hand, there are a number of possible different cathodic reactions reliant on the specific circumstances.

The reactions presented in Eqs. 3, 4 and 5 depict the normal cathodic reactions that take place in aqueous media. Eq. 3 represents the hydrogen reduction, which, due to the availability of hydrogen ions, is a common reaction in acidic and neutral media. In acidic media oxygen is reduced as depicted in Eq. 4, whereas in neutral or basic environments Eq. 5 is followed. Usually, metal ion reduction and metal deposition (Eqs. 6 and 7 respectively) are not allied with spontaneous events; instead they are reported in the case of specific industrial and chemical processes.

During the transition of metal ions to the solution, the metallic surface has an excess of negative charges while the solution shows an excess of positive charges, creating an electric field and a potential difference between the metal and the solution. This excess of negative charges attracts the metallic ions to the surface. This is the phenomenon behind the formation of the so-called double-layer. The double-layer can be extremely useful for the classification and ranking of several metals in a scale called Electromotive Series because the layer potential is assessable and is specific for all the electrode reactions. A short example of this series presenting some of the main metals is shown in the following table:
Table 2 – The Electromotive Force Series (adapted from: [48])

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>Standard potential (V)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au^{3+} + 3e^{-} → Au</td>
<td>1.50</td>
</tr>
<tr>
<td>Pt^{2+} + 2e^{-} → Pt</td>
<td>1.20</td>
</tr>
<tr>
<td>Ag^{+} + e^{-} → Ag</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu^{2+} + 2e^{-} → Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>2H^{+} + 2e^{-} → H₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni^{2+} + 2e^{-} → Ni</td>
<td>-0.25</td>
</tr>
<tr>
<td>Fe^{3+} + 2e^{-} → Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cr^{3+} + 3e^{-} → Cr</td>
<td>-0.74</td>
</tr>
<tr>
<td>Zn^{2+} + 2e^{-} → Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ti^{2+} + 2e^{-} → Ti</td>
<td>-1.63</td>
</tr>
<tr>
<td>Al^{3+} + 3e^{-} → Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Mg^{2+} + 2e^{-} → Mg</td>
<td>-2.37</td>
</tr>
<tr>
<td>Li^{+} + e^{-} → Li</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

¹potentials are relative to the standard hydrogen electrode (SHE) as an arbitrary reference;

In general, the Electromotive Series represents a worthy guideline for preliminary corrosion studies. However, since the Standard Hydrogen Electrode (SHE) is not easy to manipulate, generally, for the practical measures of potential other reference electrodes are used. Since, the alteration of the test solution may change the relative potentials of different materials, more realistic series based on real solutions were created and are known as Galvanic Series. Basically, when two metals are immersed in an electrolyte, while electrically connected, the less noble will experience galvanic corrosion. On the whole, both series are in good agreement and, in general, regarding to the rank in the series, the lower the potential the higher the tendency of that metal to corrode. Nevertheless, there are some exceptions such as the cohesive and adherent oxide layer that forms on the surface of titanium when immersed in a 3% NaCl solution for example. This layer effectively shields it from deterioration shifting the potential from negative to positive,
making it the most corrosion resistant structural metal known, with a potential even nobler than silver.

2.3.1.2. Measures and evaluation of corrosion

The corrosion stability of uncoated metal is traditionally described by its corrosion rate, which is a measure of the material weight loss per time and area, and is usually represented as mg/day/dm²

day [15]. This non-electrochemical method is applicable to any metallic sample. Other methods, like determining the solution ions and monitoring of gas evolution, are also frequently applicable but are only suitable for corrosion processes which release corrosion products soluble in the electrolyte and produce gases, respectively. For magnesium and magnesium alloys, all three methods are suitable whenever the tests are performed in aqueous chloride solutions.

To determine the corrosion rates, electrochemical techniques are often used. The corrosion current is determined and then correlated with the corrosion rate considering a previously known corrosion mechanism and the Faraday law. The corrosion current cannot be measured straight away, since at open circuit potential (OCP) all the electrons generated in the anode are consumed in the cathode, and so, no net current runs from the system. Nonetheless, the corrosion current can be determined by electrochemical impedance spectroscopy (EIS) and polarization methods.

In polarization methods, direct current (DC) is frequently used. It consists in polarizing the corrosion potential of a sample applying a cathodic potential and progressively increasing it to anodic values. Inferring the tangent (Tafel slopes) of the anodic and cathodic curves to E_corr and intercepting them enables the attainment of the corrosion current value as depicted in Figure 5. Once the corrosion current is obtained, the corrosion rate can be determined. The corrosion current can be determined only using the cathodic slope because at the corrosion potential, anodic and cathodic currents are the same, fact with considerable impact because the anodic slope is usually non-uniform and difficult to analyse.
This technique is generally used to determine the corrosion rates of several metals because it is fast and relatively simple. However, in the specific case of magnesium and magnesium alloys the use of this method to determine the corrosion rates led to some controversy in the last years because the results obtained with this technique were divergent in relation to the results obtained with other methods.

Finally, one of the most applied methods to assess the degradation behaviour of bare and coated magnesium in corrosive environments is the electrochemical impedance spectroscopy (EIS) technique. The impedance (Z), which has an equivalent physical meaning as the resistance (R), but it changes with the angular frequency (ω) of the applied potential. While in polarization methods a DC potential is applied at a constant rate, in impedance a sinusoidal potential variation at different frequencies is used, which usually ranges from $10^{-5}$ to $10^{-2}$ Hz. With this technique the contribution of several elements to the overall sample resistance (charge transfer resistance, capacitor resistance, coating resistance, etc.) can be addressed. These electrical elements can be determined by fitting the impedance spectra using different circuit models. This method is particularly suitable to investigate the corrosion performance of coated magnesium alloys and to study the coating stability.
2.4. Corrosion mechanisms of Mg and its alloys

Due to all the interest in improving the properties of magnesium alloys, and considering corrosion resistance as their major frailty, it is foreseeable to find several researches focused on the topic. In fact, there is a considerable increase in the number of publications regarding the electrochemistry and corrosion behaviour of magnesium alloys. However corrosion mechanisms are very complex and still not fully understood which explains the on-going efforts to clarify the processes involved.

Magnesium and its alloys generally show low corrosion resistance in aqueous solutions [15, 49, 50], which limits their use in engineering applications therefore protective surface coatings are essential in order to enable their safe use [51]. However, for applications such as biodegradable implants this becomes a central issue.

As with the other metals that present negative corrosion potentials, stability of magnesium hangs on the formation of a surface film that inhibits the attack of the surface when exposed to a corrosive media, but in this case, the magnesium hydroxide film produced presents a weak protective ability and is likely to breakdown.

The magnesium corrosion in aqueous solutions proceeds according to the following overall reaction [15, 49]:

\[
\text{Mg(s)} + 2\text{H}_2\text{O}(aq) \rightarrow \text{Mg(OH)}_2(s) + \text{H}_2(g)
\]

This general equation can be divided into cathodic (Eq. 9) and anodic (Eq.10) partial reactions:

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

\[
\text{Mg(s)} \rightarrow \text{Mg}^{2+}(aq) + 2\text{e}^-
\]

The pH increase due production of OH\(^-\) which favours the formation of hydroxide film by the precipitation reaction:

\[
\text{Mg}^{2+}(aq) + 2\text{OH}^- (aq) \rightarrow \text{Mg(OH)}_2(s)
\]

The prime corrosion product formed is magnesium hydroxide (Eq. 11) however different environments will lead to further types of corrosion products, for example carbonates and hydrate carbonates (when in the presence of carbonic acid or CO\(_2\) in water) or sulphites and sulphates (when in the presence of diluted sulphuric acidic or sulphur containing contaminants).
From the analysis of the previous equations it can be observed that magnesium corrosion will not be considerably dependent on the environment’s oxygen concentration [15]. These processes are illustrated on Figure 6:

![Figure 6 Reactions between magnesium alloys and aqueous environment.](image)

The corrosion behaviour of magnesium in aqueous solutions is pH-dependent; magnesium thermodynamics in aqueous solutions is described in the Pourbaix diagram (Figure 7), where the dependence of the potential on pH is plotted. The diagram shows that the divalent ion is stable in solutions until a pH value around 11. Above this point the hydroxide Mg(OH)$_2$ becomes the stable species. Subsequently, at the blood pH (~7.3 – 7.4) Mg is actively dissolved [52].

![Figure 7 Pourbaix diagram of Mg showing the range of corrosion, passivation and immunity [48].](image)
At 25°C and assuming direct contact and equilibrium between the plain metallic surface and the divalent ion, magnesium presents a very low standard potential, with a value of -2.37 V (vs. SHE) [49]. However, the electrode potential is nobler in 3% NaCl solutions: -1.63 V or – 1.38 V (vs. saturated calomel electrode (SCE) and SHE, respectively), which demonstrates that the metallic surface is not contacting directly with the electrolyte and in its place is covered by an hydroxide film that covers the surface and confers some corrosion protection in alkaline media [51].

In this context, for Mg alloy application as biodegradable implant, several corrosion mechanisms have to be addressed. They will be presented in the following sections with more detail.

2.4.1. Galvanic corrosion

Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte. This type of corrosion is observed when heavy localized corrosion of the Mg matrix is detected close to cathodic areas [49]. A distinction between external and internal galvanic corrosion can be established depending on whether the Mg is in contact with a nobler metal or whether there exist cathodic second phases or impurities in the matrix, respectively [49].

For the present work, internal galvanic corrosion represents a key issue since Mg structural characteristics can favour this type of corrosion. In pure magnesium, impurity elements with low hydrogen overvoltage such as Fe, Cu or Ni may have a negative effect on the degradation performance of magnesium even when in minor quantities, because their low solubility in Mg will ease the development of micro-galvanic cells and cause internal galvanic corrosion. Therefore, throughout alloy fabrication it is important to use highly pure material to maintain the impurity levels below the limit of tolerance [49]. Additionally, the secondary phases present in the Mg alloy can also behave as (micro-) cathodes leading to dissolution of the Mg matrix adjacent to them. Grain boundaries also represent cathodic regions to the anodic grain interior. In this case, corrosion tends to concentrate in the contiguous zone to the grain boundary until the eventual undercut and fallout of the grain [15].
2.4.2. Stress corrosion and stress corrosion cracking

Since Mg implant used as biomedical implant will be under load, corrosion under stress conditions must be addressed. In certain corrosive environments, stress corrosion cracking (SCC) usually leads to an unexpected quick failure of the sample, especially when subjected to a tensile stress. It usually progresses rapidly and is more common among alloys than pure metals. Al- and Zn-containing alloys were reported to have high predisposition to SCC \[29\] while Zr- and rare earth-containing alloys show in-between SCC susceptibility.

Studies regarding this type of corrosion claimed that, depending on the medium, chemical composition and structure of the Mg alloy, intergranular and transgranular SCC was observed \[29\]. Intergranular cracking is continuous and involves only electrochemical processes where dissolution of the matrix adjacent to the grain boundaries is observed and the consequent stress pulls the metal apart. On the other hand, transgranular cracking was found to be discontinuous and comprising mechanical and electrochemical processes. Pits and notches caused by electrochemical processes result in brittle fractures, cracking after high stress tensions. The crack stops at barriers, for example grain boundaries, and continues once the obstruction is removed by electrochemical attack. Hydrogen embrittlement was also reported to be responsible for SCC \[29\].

2.5. Progresses on surface modification of magnesium alloys

In order to provide sufficient time for tissue healing, the magnesium-based implants should maintain their mechanical integrity for more than 12 weeks. However, current magnesium alloys degrade too fast in human body and fail before the tissue heals, hampering their applications as bioabsorbable orthopaedic implants. Therefore suitable strategies need to be developed to tailor their degradation rates. To enhance the corrosion resistance of magnesium alloys and to avoid galvanic corrosion two main routes can be followed: improving the corrosion resistance of bulk materials or applying surface modification treatment in a way that inhibits electric contact between the substrate and the Mg sample surface. Various technologies exist to produce surface coatings, \[51\] nevertheless several of them confer permanent protection and consequently are not suitable for biodegradable implants. Up to now, only a few surface treatments for Mg alloys to be used as biomedical applications were described in literature \[45, 53, 54\] and cover methods such as chemical conversion treatment, ion implantation, anodic oxidation and micro-arc oxidation. A more comprehensive review of the all possible methods is available at \[51\].
Chemical conversion treatment is a process where the metal is immersed in a solution which contains certain compounds that react by forming a film. The most common conversion coating processes for magnesium alloys are based on phosphate [55, 56], chromate [57], and fluoride [58 - 60] baths. This method is cheap, easy to operate and especially suitable for treatment of samples with a complex architecture resulting in a uniform coating [61], the coatings formed by this process improve the corrosion resistance and offer wear protection in some degree. However, these types of coatings are usually described as pre-treatments since the performance of magnesium alloys coated only by these methods is usually insufficient for a series of applications. This is mostly related to the morphology of the prepared layer which is usually cracked and porous.

Ion implantation is a surface modification technique by which ions of a material are accelerated in an electric field and impacted into another material (metal, polymer and ceramic). Gaseous plasma immersion ion implantation is used to produce a layer on the magnesium alloy surface to prevent the attack from the aggressive environment. Up to now, oxygen, hydrogen and nitrogen have been experimented [62 - 64]. As the modified layer formed by plasma immersion ion implantation is considerably thin which, depending on the applied voltage and temperature on the sample can range from only several tens to several hundred nanometers, this method can only improve the corrosion performance of the treated samples to some extent.

Anodization is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of the metal parts, which constitute the anode electrode of the electrical circuit [65], resulting in enhanced corrosion and wear resistance. The composition of the anodized coatings is complex and generally consists of two layers with thicknesses ranging from 10 to 50 μm [65], the inner layer is thin and dense whereas the outer layer is thick and porous, usually requiring a sealing treatment [66]. In magnesium and magnesium alloys, the main phase in the anodized coating is constituted by magnesium oxide. However, the precise composition is determined according to the substrate, processing parameters, electrolyte, and temperature. Changes in the processing parameter will induce dramatic variations in the structure, tribological properties and adhesion of the coating. Zhang et al. studied the corrosion response of anodized AZ91 magnesium. In a 3% NaCl solution, the treated sample presents better impedance response comparatively to the untreated sample [65]. Chloride ions aggressively attack the oxide films therefore the anodized sample is very sensitive to pitting corrosion in this environment.

More recently, plasma electrolytic oxidation process (PEO) is being widely used to coat magnesium alloys. Besides PEO, this coating technique is also known as anodic oxidation with
spark discharge, micro-arc oxidation, anodic spark deposition, or plasma-chemical oxidising [67]. This process is a particular type of anodisation performed at quite high voltages (higher than the dielectric breakdown voltage of the oxide) [68] on a metal sample immersed in an alkaline based electrolyte containing chemicals such as phosphates, silicates, hydroxides, fluorides [69 - 73] which leads to the formation of oxygen plasma in the electrolyte near the substrate surface. Due to the high temperatures reached within the plasma during the sparking phenomenon, the metal surface partially melts and reacts immediately with the oxygen present, producing a well-adhered crystalline, thick (between 10 and 100 μm) and ceramic oxide coating on the surface of the metal with an average growth rate of 1 – 5 μm/min, providing excellent corrosion, wear and abrasion protection [69, 74]. Plasma-electrolytic oxidised surfaces are composed by different layers with distinct levels of porosity (figure 7): a compact barrier layer and two oxide ceramic layers. The loose outer layers are highly porous and can serve as a base for further painting, while the inner one has low porosity preventing corrosion [75]. Compared with the coating formed by anodisation, the coatings prepared by PEO usually show smaller pores and lower porosity and bond more strongly with the substrate. The PEO treatment is easy to conduct and can produce high quality coatings. However, owing to the upper porous coating layer, the corrosion protection granted by this procedure is not sufficiently good to be used as a unique process, consequently a sealing process is generally mandatory to attain the required performance [76]. Conversely, this method presents the advantage of being able to provide protective coatings free of toxic waste (depending on the followed method), and is sufficient to cover and protect complex shaped substrates and different metals in only one pass [76, 77].

![Figure 8](image.png)

**Figure 8** Schematic description of a ceramic coating prepared by PEO process. In this particular example the layers of a MAGOXID coating are shown (adapted from [78])
Since current densities and the history of film formation do not affect the breakdown voltage markedly, the anodised sample can be coated in another solution and the final voltage (for the new electrolyte) can be reached. This is called a two-step PEO where the corrosion resistance of the anodic coatings can be further improved [72].

In conclusion, generally it is possible to tailor the degradation rate of magnesium and its alloys by surface modifications. The surface treatments that result in degradable coatings, frequently result in a reduction in the initial degradation rate, and lead, after some time, to corrosion of the substrate material. Yet, the coating (and substrate) might behave differently in vitro and in vivo, therefore once a suitable process is established, its in vitro and in vivo performance must be carefully studied. When used as a biodegradable implant material, besides the corrosion resistance the mechanical properties of the Mg alloys need to be addressed. Thus, high purity Mg which has a high corrosion resistance is not strong enough to meet the mechanical requirements. This is also true for some of the often investigated cast alloys.
3. Materials and Methods

3.1. Samples

Two different magnesium alloys, WE54 and AZ31 were used for characterization of the corrosion response in NaCl and Hank’s solution. For the PEO treatment the studies were performed on AZ31.

WE54 samples used in this work were obtained from Magnesium Elektron Company while AZ31 samples were obtained from Goodfellow. For both alloys the test coupons were obtained from extruded cylinders. Wrought alloys were chosen instead of casting alloys because they provide better advantages in terms of obtainable strength and toughness [73]. The nominal compositions of the magnesium alloys used are summarized in table 3.

<table>
<thead>
<tr>
<th>ASTM designation</th>
<th>Nominal Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
</tr>
<tr>
<td>WE54</td>
<td>4.8 – 5.5</td>
</tr>
<tr>
<td>AZ31</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Minimum content

3.2. Solutions

For the corrosion investigation on these alloys, 0.05 M NaCl solution with a pH of 5.45 ± 0.09 and two types of physiological solutions were used: Hank’s balanced salt solution at 37°C and room temperature with an average pH of 7.44 ± 0.17 and Simulated Body Fluid (SBF) at room temperature with a pH of 7.31 ± 0.23. NaCl is a test solution commonly used in corrosion studies and up to now the corrosion process of magnesium in this standard saline solution has been widely studied [15, 49, 52, 74 – 76]. Hank’s solution and simulated body fluid (SBF) are standard aqueous solutions, which simulate the ion concentration of human blood but do not contain larger particles such as proteins, lipids or blood cells and have been used to assess the biocompatibility of biomaterials. For a better comparison, the ionic composition of blood’s
plasma, Hank’s solution and SBF is given on table 4. All solutions were prepared with Millipore® water and p.a. reagents.

**Table 4** Ionic composition of Hank’s balanced salt solution, simulated body fluid (SBF) and blood plasma [77]

<table>
<thead>
<tr>
<th>Solution</th>
<th>Composition in term of ions (mmol/l)</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>H₂PO₄⁻</th>
<th>HPO₄²⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hank’s</td>
<td></td>
<td>142</td>
<td>5.8</td>
<td>0.8</td>
<td>145</td>
<td>4.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>SBF</td>
<td></td>
<td>142</td>
<td>5</td>
<td>1</td>
<td>131</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Blood plasma</td>
<td></td>
<td>142</td>
<td>3.6-5.5</td>
<td>1</td>
<td>95-107</td>
<td>27</td>
<td>0</td>
<td>0.7-1.5</td>
<td>1</td>
</tr>
</tbody>
</table>

3.3. Experimental Conditions

3.3.1. Experimental Techniques

In this section some introductory material of the techniques used in the experimental work will be presented: monitoring of the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS).

3.3.1.1. Open Circuit Potential

When there are several reactions taking place on an electrode, it will show an intermediate potential between the equilibrium potentials of cathodic and anodic reactions, potential that corresponds to the intersection of anodic polarization curve of metal with the cathodic polarization curve. In electrochemistry, a potential of this type is designated as mixed potential, but in the particular case of corrosion it is referred to as the corrosion potential. In the case where metal will not corrode, the potential measured is the actual equilibrium potential of the metal. The open circuit potential is a parameter that is easily determined experimentally, only needing to make the direct measurement of the electrode potential in relation to a reference electrode.

Some common cases in which there are marked variations in corrosion potential over time are:
- Dissolution of an oxide film – Many metals and alloys have a thin film of oxide on its surface. When a metal in these conditions is immersed in a corrosive solution, the dissolution of this film can occur. This step is usually followed by a shift of the potential for more negative values until it reaches a value at which the system remains stable.

- Passivation film formation – In some cases a passive or a pseudo-passive film of oxides, carbonates or other may be formed on the metal surface. In such cases, when adding anodic inhibitors, the potential shifts to less negative values, showing at the end a more noble potential.

- Galvanic pairs – When there is a galvanic couple the set shows a potential near to the more active metal. It oxidises, cathodically protecting the nobler metal, which sees its potential getting lower in relation to its corrosion potential.

- Other factors – Variations of the test environment also affect the corrosion potential. Parameters such as pH, dissolved oxygen concentration, temperature, agitation, concentration of metal cation and concentration of aggressive and passivating ions.

### 3.3.1.2. Electrochemical Impedance Spectroscopy

A significant proportion of the work presented in this thesis was performed by Electrochemical Impedance Spectroscopy (EIS).

Actually, EIS can be considered as a valuable technique for kinetic and mechanistic characterization of electrochemical systems as it obtains, if measured over an infinite range of frequencies, all the information possible to achieve by electrical means. During EIS experiments, a small amplitude AC signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rates, dielectric properties, compositional influences on the conductance of solids, electrochemical mechanisms, mass transport, detection of localized corrosion, and reaction kinetics can all be determined from these data. [78, 79] This technique is easy to apply, however, for the data processing there is a need to use appropriate software.

According to Macdonald [80], the concept of electrical impedance was introduced by Oliver Heaviside in the 1880s and its development in terms of vector diagrams and complex representation appeared shortly afterwards by A. E. Kenelly and especially C. P. Steinmetz.
Currently there are several books and review articles devoted to the technique and its different applications [80 - 82].

Obtaining experimental impedance response has evolved with the progress of computer systems and analogic and digital electronic systems. Initially measurements were made manually, point by point using Wheatstone bridges or oscilloscopes (analysing Lissajous figures). Nowadays, besides that, lock-in amplifiers and frequency response analyzers are used, apparatus that give an automatic response for a wide frequency range.

3.3.1.2.1. Impedance Definition

The concept of impedance is based on Ohm’s law (Eq.12) that correlates the resistance of a circuit component with the flow of electrical current.

\[ R = \frac{V}{I} \]  

Eq. 12

where \( R \) is the electrical resistance, \( V \) is the potential and \( I \) the electrical current that passes in the circuit.

Since Ohm’s law use is limited to d.c., where the resistance follows Eq. 12 for any voltage value, for applied AC voltage signals the concept of impedance (\( Z \)) was created:

\[ Z = \frac{V(t)}{I(t)} \]  

Eq. 13

Unlike resistance, impedance is not affected by the same limitations as the electrical resistance.

EIS is usually measured by applying a small excitation signal under the form of a sinusoidal wave potential signal:

\[ V_t = V_0 \sin(\omega t) \]  

Eq. 14

in which \( V_t \) is the potential expressed as a function of time \( t \), \( V_0 \) represents the signal amplitude and \( \omega \) is the angular frequency. The system will respond with a current signal, \( I_t \) given by:

\[ I_t = I_0 \sin(\omega t + \Phi) \]  

Eq. 15
Where \( I_0 \) is the amplitude of the current signal and \( \phi \) is the shift in phase between the two signals (phase angle). Thus, the expression 13 can be rewritten enabling the calculus of the system’s total impedance:

\[
Z = \frac{V_1}{I_1} = \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)}
\]

Eq. 16

The system’s impedance can also be represented as vector, \( Z \). This vector might also be characterized as a complex function with real and imaginary components. According to Eulers relationship, \( e^{i\phi} = \cos \phi + j \sin \phi \), the impedance can then be described as a complex number:

\[
Z = \frac{V_0 e^{i\omega t}}{I_0 e^{i(\omega t + \phi)}} = Z_0 e^{i\phi} = Z_0 (\cos \phi + j \sin \phi)
\]

Eq. 17

In electrochemical studies the impedance spectrum can be present either as a Nyquist plot or as a Bode plot.

The Nyquist plot is a cartesian chart where the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis. Each point on the Nyquist plot represents the impedance at one frequency, however it does not provide enough information to tell what frequency was used for each data point. Detailed information such as kinetic data and polarization resistance results can be directly obtained from the analysis of these plots.

In more complex electrochemical systems, the representation of results in polar coordinates (Bode plot) becomes more useful. On Bode plots the impedance is represented with \( \log|Z| \) and phase angle on the Y-axis as a function of \( \log \omega \) in the X-axis, where the angular frequency \( \omega \) appears as the independent variable.

The electrochemical impedance response observed when a potential perturbation is applied to an electrode/electrolyte interface is simulated with the response of the electric circuit components (i.e. resistors, capacitors and inductors).

In the case of a pure resistance, Ohm’s law is applicable. Since the conditions specified in the beginning of this section are verified, the impedance of a resistance is directly proportional to the resistance [83]:

\[
Z_R = R
\]

Eq. 18
In figure 9 it is possible to observe that the resistance corresponds to a single point in the real axis at the distance $R$ from the origin in the Nyquist plot, while in the Bode plot two horizontal lines in the $\log|Z|$ and phase angle plot are represented.

For a capacitor, the analysis must start with the equation that follows:

$$q = CV \quad \text{Eq. 19}$$

which, in terms of current, means:

$$I = \frac{dq}{dt} = C \frac{dV}{dt} \quad \text{Eq. 20}$$

After some mathematical manipulation we can obtain a simplified expression for the impedance of a capacitor (Eq. 21), which has only the imaginary component and is inversely proportional to the perturbation frequency and capacitance ($C$).

$$Z_C = \frac{1}{j\omega C} = -\frac{1}{\omega C} \quad \text{Eq. 21}$$

In the Nyquist chart the capacitor response appears as a straight line along the imaginary axis ($Z_{\text{real}} = 0$) that converges to the origin whereas in the Bode plot a straight line with a slope of -1 for $\log|Z|$ and an horizontal line at -90° for the phase angle are obtained.

For an inductor, the impedance is directly proportional to the perturbation frequency and inductance ($L$), having only a complex component:

$$Z_L = j\omega L \quad \text{Eq. 22}$$
In the Nyquist diagram, the impedance increases with the frequency, whereas in the Bode plot the slope of the log|Z| chart is 1 and the phase angle is +90°, precisely the opposite of the capacitor plots.

Based on these basic examples, the same concepts can be extended to the analysis of complex electrochemical systems where several resistors and capacitors are associated in series or parallel. Figure 10 shows an example of a system commonly found in electrochemical analysis.

![Nyquist and Bode plots for R (RC) circuit](image)

**Figure 10** Nyquist and Bode plots for R (RC) circuit [80].

The graphs represent the complex representation of impedance response of a R(RC) circuit, with a resistor ($R_0$) in series with another resistor connected in parallel with a capacitor. The impedance of this system is given by:

$$Z = R_0 \frac{R}{1+j\omega CR}$$  \hspace{1cm} \text{Eq. 23}

The next table shows the basic elements of an electric circuit and how they respond to alternating current:

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Impedance Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td><img src="image" alt="Resistor" /></td>
<td>$Z = R$</td>
</tr>
<tr>
<td>Capacitor</td>
<td><img src="image" alt="Capacitor" /></td>
<td>$Z = \frac{1}{j\omega C}$</td>
</tr>
<tr>
<td>Coil / Inductor</td>
<td><img src="image" alt="Inductor" /></td>
<td>$Z = j\omega L$</td>
</tr>
</tbody>
</table>

---

40 | 86
In terms of results analysis two different approaches can be followed: the first makes use of the “equivalent electrical circuit” to control the electrochemical behaviour of the system, while the second is purely based on the analytical treatment of the impedance concerning the development of highly complex mathematical models based on the kinetics of the reactions involved [79, 84]. For the data analysis of this work the first approach will be used.

As an example the impedance spectra presented on Figure 10 can be fitted by the R(RC) circuit depicted on Figure 11, modelling, for instance, a corrosion process controlled by charge transfer on a metallic surface.

![Figure 11 Equivalent circuit for the interpretation of the impedance plots of Figure 10](image)

For this example $R_\Omega$ represents the ohmic resistance (also represented as $R_0$ or $R_s$) which comprises the electrolyte resistance, the electrical wire resistance and the electrodes internal resistance. The last two terms are negligible when compared to the former, because wires and electrodes have resistances several orders of magnitude lower than the electrolyte. Hence, the ohmic resistance is usually defined as the solution resistance.

$R_{ct}$ is the charge transfer resistance, the faradic component of the current, which, in terms of representation, is the diameter of the semi-circle R. It can be defined as the resistance associated with the electron addition or removal.

$C_{dl}$, the double layer capacitance, is defined as the capacitance created when separation of charges on both sides of metal-electrolyte interfaces (the electrochemical double layer) occurs. It will behave like a parallel plate capacitor which by consecutive charges and discharges will enable the current to pass in a discontinued form. This double layer capacitance ($C_{dl}$) depends on the double layer thickness, on the dielectric constant and on the ionic concentration of the electrolyte and can be calculated using the expression 24:

$$C_{dl} = \frac{1}{\omega^* R_{ct}} \tag{Eq. 24}$$

$\omega^*$ is the angular frequency at the point with absolute maximum ordinate at the Nyquist Plot.
However, the previous example will only fit very simple systems. Common systems will have several processes straddling and overlapping in the work frequency range thus different programs for fitting analysis were developed, enabling, by using several algorithms, the automatic calculation of the parameters.

The choice of an equivalent circuit that characterizes with high precision the system is usually the main challenge in the fitting process of an electrochemical system. The proper characterization will always require experience and previous knowledge of the electrochemical reactions taking place at the electrode surface.

In truth the deviation from the ideal behaviour makes more difficult the impedance spectrum data analysis. The semi-circle obtained in the Nyquist plot for the overall frequency domain is never perfect, as in Figure 10, generally looking depressed. The level of depression will diverge from system to system.

This type of depression was firstly described by Cole and Cole [85], who in their study of dielectric constants also used complex representations, later named as Cole-Cole Depression. This concept was later adjusted to electrochemical systems by a number of different authors [83].

Looking at the impedance spectra plotted in Figure 10, there is only one electrochemical process modelled by the equivalent circuit represented on Figure 11. For this system we can outline one time constant ($\tau$):

$$\tau = R_{ct} C_{dl}$$

Eq. 25

The depressed semi-circles whose centre lies below the real axis are explained by considering that the time-constant $\tau$ is not a constant value, being distributed around an average value, $\tau_0$. The explanation for the occurrence of dispersion of time constants is mostly related with the heterogeneity of the electrode surface by considering it as being composed by big number of small adjacent electrodes, each with its own values of $R_{ct}$ and $C_{dl}$ and, therefore, its own value of $\tau$ [83].

A different approach to deal with the depression in EIS measurements relies on the Constant Phase Element (CPE) component. This element is similar to a capacitor but phase angle differs from 90°.

The use of CPE is only based on empirical considerations and does not have any theoretical support. The mathematical simplicity of this model combined with the fact that it is a separate circuit element, (contrasting with the case of Cole-Cole depression, which affects the overall time-
constant and, consequently, R and C) made it generally accepted for the fitting of experimental data.

Overall, both methods give analogous results for the depression problem. This can be verified by solving the equations for the impedance of a R(RC) circuit considering the Cole-Cole depression (Eq. 26) substituting the capacitor by a CPE (Eq. 27)

\[
Z_{\text{Cole}} = R_0 + \frac{R}{1+(j\omega \tau)^{1-\alpha}} \quad \text{Eq. 26}
\]

\[
Z_{\text{CPE}} = R_0 + \frac{R}{1+R_Y [(j\omega)]^{n}} \quad \text{Eq. 27}
\]

For which \( n=1-\alpha \) can assume any value approximately above 0.75 and up to 1.

Since the phase of a CPE can be altered, the element becomes very versatile and, depending on the \( n \) value, can represent the response of any other passive component in an electric circuit such as resistors \( (n=0) \), capacitors \( (n=1) \) or inductors \( (n=-1) \). A CPE can also simulate diffusion controlled processes, normally fitted with elements called Warburg diffusion elements, when \( n=0.5 \). These points become particularly useful to determine circuit elements when using automatic fitting methods because, by introducing indefinite elements such as CPEs, the calculation algorithm will attribute values to the \( n \) parameter, hence defining weather a given element of the circuit should be represented by a resistor, a capacitor or an RC circuit with depression. Actually, it is possible to create an equivalent circuit consisting only of CPEs that will give a good mathematical result for any electrochemical processes, even lacking of proper physical sense. Therefore, CPE may be used as an initial step of fitting in order to define which circuit elements should be integrated in the model.

The study of increasingly complex systems lead to the appearance of wide range of EIS spectra and sometimes it is difficult to discern between a valid outcome and a result from an experimental error. The validity of the EIS measurements will depend on these four conditions: [79, 83].

- Causality – The response of the system must be due only to the perturbation applied;
- Linearity – The relation between perturbation/response of the system must be described by a set of linear differential laws. This condition requires that impedance must be independent of the perturbation magnitude, which means that EIS measurements should be conducted at potentials...
close to OCP where the response is linear (the perturbation shall be in the vicinity of 10 to 20 mV around the corrosion potential);

- Stability – The system must be stable, returning to its original state after the perturbation is stopped;

- Impedance must be finite-valued at $\omega \to 0$ and $\omega \to \infty$ and must also be a continuous function with finite values for all the intermediate frequencies.

If the above conditions are not verified the results may not be valid leading to a misinterpretation of the physical properties and system’s conditions.

### 3.3.1.3. Surface Characterization

#### 3.3.1.3.1. Scanning Electron Microscopy

The Scanning Electron microscopy (SEM) is currently one of the most widely used tools in research and industry. It enables the observation and local characterization of heterogeneous organic and inorganic samples at the micrometre and sub-micrometre scale. Materials’ surface topography (with three-dimensional-like images of the surfaces of a very wide range of materials), chemical composition and crystallography can be accessed using this technique [86].

The operating principle of the SEM involves the scan of the sample surface, using a finely focused electron beam, controlling the brightness at each point of the obtained image which is acquired in accordance with the signal emitted by the sample. The fundamental quality parameter of SEM is its maximum resolution, which corresponds, from the instrumental point of view, to the minimum diameter of the electron beam.

The maximum spatial resolution of images in SEM commercial devices is around 2 to 5 nm, but resolutions higher than 1 nm have been achieved in advanced research instruments [87].

In the usual mode of operation, accelerated electrons transport considerable amounts of kinetic energy, which can be dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (used to produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (used to determine crystal structures and orientations of minerals), photons (characteristic X-rays used for elemental analysis and continuum X-rays), visible light, and heat.
Secondary electrons (low energy electrons - <50 eV) originated from the interaction process of primary and BSE with the electrons with lower binding energy, are most valuable for assessing morphology and topography on samples. The sample's topography will present a similar look to what would present under direct observation. BSE are used to illustrate contrasts in composition of multiphase samples. X-ray results from the inelastic collisions of the incident electrons with electrons in discrete orbitals of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element that is "excited" by the electron beam, this is the basic principle of Energy-Dispersive X-ray Spectroscopy (EDS) [88].

EDS is a technique based on the following working principle: a semiconductor detector simultaneously gathers the entire spectrum of X-rays emitted by the sample; after processing, the
spectrum is transmitted to a multichannel analyser which, controlled by a microprocessor, allows the immediate visualization of the spectrum and its treatment.

The detector Si(Li) uses the principle of the photoelectric effect. After passing through a thin beryllium window (few μm), the X-rays reach the detector and produce the electrons motion from the valence band to the conduction band, generating some gap electron pairs.

The number of generated pairs is directly proportional to the energy of the incident X-radiation. This is a statistical process and the number of generated pairs has a Gaussian distribution with a mean value proportional to the photon energy, and a standard deviation dependent on the characteristics of the detection system and the incident photon energy.

With these systems only X-rays with energies greater than 880 eV are detectable, which limits the use of this spectrometer to detect elements starting from sodium.

SEM/EDS analysis is considered a "non-destructive" technique; X-rays do not induce sample's volume loss, property that makes it possible to study and analyse repetitively the same material.

### 3.3.1.3.2. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) provides a quantitative chemical analysis of the surface composition that can be used to analyze the elemental composition, the empirical formula and the chemical and electronic state of the constituent elements of a certain material in its “as received” state, or after some treatment.

The basic principle of the XPS technique is the photoelectric effect: XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and the number of electrons (photoelectrons) that escape from 1 to 10 nm of the material being analysed. For each and every element, there will be a characteristic binding energy associated with each core atomic orbital \( i.e. \) each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region.
The relation between the kinetic energy of the emitted electrons ($E_k$), the energy of the incident radiation ($h\nu$) and the bonding energy of the electron ($E_b$) was derived by Einstein:

$$E_k = h\nu - E_b$$  \hspace{1cm} \text{Eq. 28}

XPS detects all elements with an atomic number ($Z$) of 3 (lithium) and above. Hydrogen ($Z = 1$) and helium ($Z = 2$) cannot be detected because the diameter of their orbitals is extremely small, reducing the catch probability almost to zero [89, 90].

The poor spatial resolution of several millimetres was, until recently, one of the major shortcomings of XPS. However, recent advances in instrumentation have allowed for some constructors to offer values of spatial resolution as low as 100 μm or even 20 μm [91].

XPS requires ultra high vacuum (UHV) conditions and is a technique routinely used to study metal alloys, inorganic compounds, polymers, semiconductors, glasses, ceramics and many others.

### 3.3.2. Comparison between the two media (NaCl and Hank’s solution) and the two alloys (WE54 and AZ31)

#### 3.3.2.1. Sample preparation for Electrochemical Tests

For the first stage of this work, study and characterization of AZ31 and WE54 Mg alloys, all the samples, previously divided into small coupons, were mounted on epoxy resin after ensuring the electrical contact by gluing a copper wire to them with silver based paint (SPI®).

In order to obtain comparable surfaces and ensure the same surface roughness, the samples were polished with SiC paper up to 2400 mesh and later cleaned in acetone for 5 minutes with ultrasonic agitation and dried with a stream of air prior to the experiments. To prevent the onset of crevice corrosion between the resin, the test surface area was delimited with bee wax.

The tests were carried out in a typical three electrode system, in which the sample (~1 cm$^2$ exposed area) constitutes the working electrode (WE), the saturated calomel electrode (SCE) constitutes the reference electrode (RE) and the counter electrode (CE) a platinum coil (Figure 13).
The electrochemical impedance spectroscopy measurements were carried out in a Gamry Ref 600. The scans were performed at different immersion times after reaching a steady state open-circuit potential using a sinusoidal potential perturbation with AC amplitude of 10 mV over the frequency range $10^5$ Hz – $10^{-2}$ Hz with 8 points per decade. The results were analysed with the ZView2 Software.

### 3.3.2.2. Analytical and Surface Characterization

X-Ray Photoelectron Spectroscopy (XPS) measurements were performed using a Microlab 310 F (Thermo Electron – former VG Scientific) equipped with a Mg (non-monochromated) anode and a concentric hemispherical analyzer.

The XPS analysis was performed under pressures below $5 \times 10^{-9}$ mbar, using an Al radiation (non-monochromator). The spectra were taken in constant analyser energy (CAE) mode = 30 eV and accelerating voltage of 15 kV. The quantification was determined after peak fitting. The peak...
fitting function used was a Gaussian – Lorentzian product function and the algorithm was based on the Simplex optimization as used in the Avantage® software.

Microstructural characterization of both alloys was carried out by scanning electron microscopy (SEM). For these tests the surface of the samples was prepared according to the same basic polishing sequence as the samples for the electrochemical tests. The SEM analysis was performed after a period of immersion in the test solutions of 1 and 24h using a JEOL JSM-7001F with an Oxford INCA EDS unit for chemical composition analysis. Images and chemical composition spectra were acquired at different magnifications and points on the samples.

3.3.3. Plasma Electrolytic Oxidation treatment

3.3.3.1. Surface preparation and Pre-treatment:

The materials were cut into specimens with ~15 cm² of working area, with electrical connection provided through an aluminium wire. Each process was preceded by a cleaning pre-treatment in order to remove organic, inorganic and/or metallic impurities that considerably influence the protectiveness and effectiveness of the coating. Therefore, the exposed surface was ground to 500 and 800 grit SiC paper using water and ethanol as a lubricant, respectively. It was then rinsed in deionized water and dried in air. In order to obtain a stable current transfer from the sample to the electrolyte, a threaded hole of 2.5 mm diameter was made on one of the lateral sides of the cylindrical samples, and such samples were screwed to an aluminium wire (Figure 9), properly isolated, which carried the current.

The sample was then immersed in methanol and degreased in 60 g L⁻¹ NaOH solution at 60°C for 60 s, rinsed with deionized water, etched in 0.5 M NH₄F at 80°C for 10 minutes (process that leaves the sample surface covered with MgF₂, becoming slightly darker) and finally rinsed with deionised water during 30 s.
3.3.3.2. PEO treatment and characterization

PEO treatment was carried out using a 300V/2A power supply, produced by Elektrotech, Poland, where voltages between 0 and 300 V can be obtained. Three different solutions were used as electrolyte, which can be divided as highly concentrated solutions (M2) or low concentration solutions (M3 and M4). These solutions were prepared from deionised water and high purity chemicals, and were continuously stirred during treatment; their chemical composition is disclosed on table 5. The coatings were formed in a 1000 ml double-walled glass cell. A heating plate was used to keep the electrolyte temperature close to 25°C. Two rods of graphite, of dimensions 25 cm, were used as counter electrodes, both of them positioned on opposite sides relative to the sample in order to ensure a homogeneous current distribution and, thus, a homogeneous coating over the entire surface. Two different routes were followed as described on Figure 16. The general coating procedure is described in the Appendix. After being anodized, specimens were rinsed with deionized water and dried in warm air.

Figure 15 The two approaches followed during the PEO treatment: (a) Step and (b) pulse current programmes
Table 6 Chemical composition of electrolyte solutions used for the PEO treatment

<table>
<thead>
<tr>
<th>Composition (g/L)</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M2 50°C</td>
</tr>
<tr>
<td>NaF</td>
<td>40</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$</td>
<td>50 mL/L</td>
</tr>
<tr>
<td>KOH</td>
<td>-</td>
</tr>
<tr>
<td>Na$_3$PO$_4$.12$H_2$O</td>
<td>-</td>
</tr>
<tr>
<td>NB-2$^2$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^1$Solution of sodium silicate – Na$_2$O x nSiO$_2$ x nH$_2$O (water glass)

$^2$Tetraethylenepentamine + formaldehyde

The thickness of the coated samples was firstly assessed using an Elcometer® coating thickness gauge.

The electrochemical behaviour of anodized samples was studied in simulated body fluid, using the previously mentioned (see section 4.4.1) three-electrode setup.

The coating morphology was examined by scanning electron microscopy, using a ZEISS EVO50 instrument equipped with EDS analysis to assess the coating composition. Cross-sections of the PEO coatings were prepared (at MEG, Warsaw) in order to enable the analysis of the thickness and composition of the anodized layer and also to investigate whether this coating is uniform or if it includes pores.
5. Results

5.1. Comparison between the two media (NaCl and Hank’s solution) and the two alloys (WE54 and AZ31)

The toxicity of a metallic material depends not only on the composition and toxicity of the constituent elements but also on its corrosion and wear resistance [44]. Metal ions released from corroducible alloys to the surrounding tissues, may cause biological responses in short or prolonged periods. In a saline environment, magnesium-based alloys would be degraded to magnesium chloride, oxide, sulphate or phosphate [5], the same occurring in Hank’s solution.

AZ31 magnesium alloys are characterized by low cost of production and satisfactory mechanical properties. They contain 3 wt% aluminium and 1 wt% zinc. In physiological concentrations, zinc is an essential trace metal which is associated with many intra- and extracellular processes in mammals and has toxic effects only in high concentrations [92, 93]. Aluminium is a non-essential element and can have toxic systemic effects when the normal excretion is impaired. Recently, in an in vivo study undergone by Willbold et al. was observed that 3 and 6 months post implantation of an AZ31 magnesium screw in the hip bone of sheeps, the same was yet present and in a macroscopically good condition and shape. More importantly they found out that Mg-implants did not cause any obvious cellular immunological response in the neighbouring tissues both after 3 and 6 months [92]. Furthermore, Gu et al. [44] also concluded that in comparison to several other binary magnesium alloys, the Mg-Al alloy revealed a better cytotoxicity response to all the tested cell lines.

WE54 magnesium alloys containing zirconium and rare earth (RE) additions are known to have excellent mechanical properties at elevated temperatures and high strength [94, 95], representing the actual pinnacle in Mg alloy evolution. In addition, WE54 has been shown to be a suitable candidate as an implant application material due to its good corrosion resistance in aqueous solutions which is ascribed mainly to the beneficial influence of the alloying element Y [10, 24, 39, 96].
Different corrosion morphologies have been reported for rare earthed alloys. Zucchi et al., for instance, [75] observed galvanic corrosion between the magnesium-rare earth intermetallic compounds and the magnesium matrix. “Intergranular” corrosion attack after immersion in synthetic seawater solution was described in [116]. Further studies [117, 118] also report pitting corrosion in chloride solutions. Ben-Hamu et al. [119] observed preferential attack between the grain boundaries and the grain centres after selective thermal treatments, when zirconium is concentrated at the centre of the grain. These variations could be clarified if changes in yttrium distributions after different thermal treatments of the alloy or different pH and chloride ion concentrations in the test solutions [70] are considered.

5.1.1. Open Circuit Potential Results

Figure 16 shows the evolution of Open Circuit Potential (OCP) (vs. SCE) for both magnesium alloys when immersed in 0.05 M NaCl (room temperature) and Hank’s solution (room temperature and 37°C).
For both alloys and conditions presented the OCP values remained relatively stable, suggesting film formation or passivation. From the results it is also worth noting that WE54 exhibits a lower open circuit potential for all the conditions, remaining relatively stable at around -1.58 V throughout the immersion period. Accordingly to literature it is generally expected that the addition of RE to magnesium alloys induces an increase of the potential to more positive (nobler) values [16, 97, 98]. This drift was observed by Rosalbino et al. [99] for AE91(Ce) and AE91(Er) alloys. It has been shown that rare elements accelerate the kinetics of Mg(OH)₂ formation during the corrosion process in aqueous media [100], acting as a barrier against further corrosion of magnesium [70]. In this work, it was observed that the presence of RE additions provoked a shift in the OCP of the alloy WE54 to more negative values, which may be due to a higher content of yttrium that presents a very low potential [52]. Petrova and Krasnovarski reported that more than 2% Y addition gives corrosion rates higher than pure magnesium and formation of Mg₄Y₅ was reported as the main reason [70, 101]. Identical trends were observed in passivating media and borate buffered solutions [102]. Furthermore, it was suggested by some authors that Zr present in solid solution, in Mg alloys, acts as cathodic inhibitor [103], therefore a more homogeneous distribution of this element in the Mg matrix can be related with the resultant negative OCP values [104, 105]. In addition, the standard potentials of most rare earth elements are very close to magnesium which highlights the need of more studies regarding this subject.

For AZ31, the presence of Al shifted the OCP to nobler values [106]. It has been reported that aluminium enrichment of the corrosion layer provides better passivation properties than Mg(OH)₂ and MgO layers usually formed during the corrosion process [107].

5.1.2. Electrochemical Impedance Spectroscopy Results

As enlightened previously, in order to identify and investigate the electrochemical reaction mechanisms (uniform versus localized corrosion susceptibility), the electrochemical behaviour of the untreated (and treated (anodised) samples) was examined by EIS. The EIS measurements with its frequency depending information allow distinguishing between different corrosion mechanisms and to assess the protecting ability of the surface corrosion products [3].

The film formed during exposure to the different electrolytes can act, according to its stability and homogeneity, as a more or less efficient electric barrier for the charge transfer. The higher the
resistance of the resultant surface layer, the higher the corrosion resistance of the film and therefore the higher will be the impedance value measured at low frequency [3].

It is worth to mention that due to the complexity of the corrosion mechanisms with uniform and localized corrosion processes occurring as well as oxide layer formation on alloys with heterogeneous microstructure it is very difficult to formulate equivalent circuit models for the impedance measurements.

Figures 17 and 18 disclose the EIS scans as Bode plots for both WE54 and AZ31 in 0.05 M NaCl and Hank’s solution at room temperature and 37ºC at different immersion times up to 24h. Depending on the frequency domain considered, the Z modulus and the phase angle curves give important information concerning the type of electrochemical processes occurring during the immersion [3].

![Figure 17 Bode plots of WE54 and AZ31 alloys immersed in NaCl for 4, 12 and 24 hours.](image-url)
Both alloys showed similar impedance spectra and a general analysis of the graphs shows that when immersed in NaCl they present resistive contributions at high and low frequencies and a capacitive region at intermediate frequencies and, when in Hank’s solution, they disclose capacitive regions at high and intermediate frequencies and resistive regions at frequencies lower than 1 Hz, [70, 108]. The high and the middle frequency loops are normally associated with either the corrosion process (possessing a double layer capacitance and a charge transfer resistance) or with mass transport through a corrosion product layer. The low frequency inductive loop has been linked with the relaxation of adsorbed species.

After immersion in NaCl the absolute impedance values at low frequencies decrease gradually for AZ31 while for WE54 they increase with immersion time, which is an indication of the better corrosion resistance of this alloy in saline solutions (Figure 19).

Figure 18. Bode plots of WE54 and AZ31 alloys immersed in Hank’s solution (pH 7.40) at (a) room temperature and (b) 37°C for 4, 12 and 24hours.
It is also worth noting that in Hank’s solution, at room temperature, an increase in time of immersion generally increases the impedance values, especially during the first 12 hours (Figure 20). WE54 showed the largest increase on impedance response (Figure 20). This trend can be explained based on a decrease in the adsorbed amount of aggressive anions forming the Hank’s solution such as Cl⁻, HCO₃⁻, H₂PO₄⁻ or HPO₄²⁻ on the electrode surface [109] and on the creation of adherent corrosion products on the sample’s surface such as magnesium hydroxide (Mg(OH)₂), as well as phosphates and carbonates [110, 111] and, in particular, hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂. These products precipitation is essentially due to saturation of solution and localized alkalization which occurs during the corrosion process of magnesium alloys [44, 112].

It is also important the fact that, for Hank’s solution, an increase in the temperature provokes a decrease of impedance values which is more accentuated for WE54 with values one order of magnitude lower (from $10^5$ to $10^3$ Ω cm², at room T and 37°C, respectively) (Figures 18 a), b) 20 and 21).

A more detailed look shows that, in Hank’s solution the existence of a surface film was suggested by the presence of a high frequency relaxation process in WE54 and AZ31 alloys, denoted by a phase lag at approximately 100 kHz which becomes more evident as the immersion time elapses. This peak was not present in NaCl. In literature, however, besides being attributed to the formation and precipitation of a film [13, 124], other authors have also argument that the phase angle is a very sensitive indicator of the localized corrosion. In their models, artificial pitting was generated on the samples. When pits had grown to a certain size, a new time constant appeared at the high frequency region [123, 125].

![Figure 19](image-url)  
**Figure 19** Evolution of |Z| with time, in the low frequency range (0.01 Hz), for WE54 and AZ31 immersed in 0.05 M NaCl
5.1.3. Compositional Analysis by X-Ray Photoelectron Spectroscopy

The chemical composition of WE54 and AZ31 after 24h exposure in Hank’s solution was analysed by XPS as shown in Figures 22 and 23, respectively. Both alloys presented a similar XPS spectra. The analysis obtained revealed the presence of magnesium hydroxides as expected and few traces of the alloying elements such as Zinc hydroxide in the AZ31. The high concentration of carbon in the film surface is common in XPS survey scanning due to the adventitious hydrocarbons from the environment [121].
The most important feature is the presence of phosphorous and calcium, present in the Hank’s solution and that seem to form part of the surface film. In both samples the total calcium content is about half of magnesium. Identical ratio was observed for phosphorous (Figures 22 and 23). The high resolution spectrum for calcium element split into two peaks as a result of spin orbit splitting. Similar results were observed in [121] with further correlation to $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ formation.

On the other hand, the formation of phosphate compounds in identical solutions and experimental conditions was assessed in literature [106] where, by X-ray diffraction Mg phosphate was found. These compounds are formed when the pH reaches values above 8 as consequence of the strong magnesium oxidation rate.

![Figure 22 XPS ionization spectra for a) Ca2p and b) P2p of WE54 immersed for 24h in Hank’s solution.](image)

![Figure 23 XPS ionization spectra for a) Ca2p and b) P2p of AZ31 immersed for 24h in Hank’s solution.](image)
5.1.4. Microscopic and Quantitative Analysis by Scanning Electron Microscopy

The SEM images obtained for both alloys before immersion (Figure 24) revealed very similar surface. For WE54 EDS mapping evidenced the presence of Mg and Y but no other alloying elements, and for AZ31 apart from Mg and O no other element was identified (Table 7).

Figure 24 SEM images of (a) WE54 and (b) AZ31 alloys before immersion.

Figure 25 SEM images of WE54 after immersion in 0.05 M NaCl at room temperature for (a) 1 and (b) 24h and in Hank's solution at 37°C for (c) 1 and (b) 24h, respectively.
Characterization of the surface oxide formed and its influence on the stability in aqueous media is a key aspect of this work.

1 hour after immersion both samples revealed localized attack at early stages with several pits and network-like cracks detected over the surface, possibly related to the galvanic couple due to cathodic intermetallic precipitates at grain boundaries. [70]. These micro-cracks seem to be more severe when the sample is immersed in NaCl. For increased immersion times, corrosion damage was characterised by an accumulation of an inhomogeneous corrosion layer as shown on images b) and d) of Figures 25 and 26. At the end of 24 hours faster accumulation of corrosion products is observed for AZ31.

After exposed to NaCl for a period of 24h the Mg alloys were both covered with a non-porous film. The corrosion layer formed in NaCl clearly shows a different morphology from those formed in Hank’s solution. The surface shows very small crystallites covering the whole surface. The crystalline products observed in this film are composed of Mg(OH)$_2$, brucite. Similar findings were described in [41, 102].

After immersion in Hank’s solution, globular precipitates were accumulated at the interface of the sample (Figures 25 and 26, (d)). Similar structures were reported on Bracci et al. study as calcium phosphate (CaP) deposition [113]. This allied with the EDS results (Table 7), which reveal the presence of Ca and P in the precipitates, points to calcium phosphates deposition in our study too.
On a different study [121] the same white globular-like particles were deposited in the magnesium sample after immersion in SBF and reported as mainly composed of hydroxyapatite and magnesium phosphate which also meets the results obtained here.

Combining the mechanical advantages of the metal with the excellent bioactivity of the calcium phosphate precipitates represents an aim of utmost importance in the current bio-implants paradigm. [113].

### Table 7 EDS results before immersion and after 24h in 0.05 M NaCl and Hank’s Solution

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Alloy</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
<td>O</td>
</tr>
<tr>
<td>Before immersion</td>
<td>WE54</td>
<td>92.5</td>
</tr>
<tr>
<td></td>
<td>AZ31</td>
<td>97.9</td>
</tr>
<tr>
<td>NaCl (room T)</td>
<td>WE54</td>
<td>41.1</td>
</tr>
<tr>
<td></td>
<td>AZ31</td>
<td>44.6</td>
</tr>
<tr>
<td>Hank’s solution</td>
<td>WE54</td>
<td>74.1</td>
</tr>
<tr>
<td>(37°C)</td>
<td>AZ31</td>
<td>7.9</td>
</tr>
</tbody>
</table>

As evidenced by EDS mapping (Table 7 and Figure 27), in NaCl the corrosion layer formed mainly consists of magnesium and oxygen with a residual precipitation of magnesium chloride. This was expected because Mg(OH)_2 corrosion layers are typical from magnesium in standard saline solutions [41]. The chloride ions also present in our samples are aggressive for the magnesium
alloy not from a passivation breakdown perspective, but because the absorption of chloride ions on the oxide films of the magnesium surface transforms Mg(OH)$_2$ into the easily soluble MgCl$_2$ [3, 131].

Then again, in Hank’s solution both alloys degraded into preferentially magnesium hydroxide, but also magnesium chloride and magnesium phosphate. Deposition of calcium phosphate is also observed (Table 7 and Figure 27). Corroborating with the results obtained here, several studies [10, 24, 27, 37, 40 - 42, 53, 114, 121] show that the layer forming in SBF during in vitro and in vivo exposure consists of amorphous calcium phosphates. Further investigations, described in [41] have shown that in SBF, corrosion layers of amorphous carbonated calcium-magnesium-apatite with a thickness of about 20 μm were formed after 5 days of immersion. When compared to other corroding metals, these layers are very thick, which indicates that they offer low protection and cannot be considered as real passive films [114].

Interestingly, in their work Rettig et al. found that calcium ions are only precipitated as calcium phosphates, therefore only when phosphates are also in solution. Oppositely, phosphates can be deposited without any calcium, precipitating also together with other ions such as magnesium, therefore, the phosphates we have in Hank’s solution, besides precipitating together with the calcium, will also form complexes with the magnesium from the substrate.

Moreover, in a study undertaken by Alvarez-Lopez et al. the high P signals (EDS) observed around the pits, that appear in AZ31 magnesium alloys after 30 minutes of immersion in phosphate-buffer solution, are an indication of the eventual correlation of phosphates with the AZ31 initial fast corrosion [13].

From the results on Table 7 we can also point that, after immersion in Hank’s solution, the corrosion layer in WE54 is considerably thinner in comparison to the same in AZ31 because a strong signal from the magnesium substrate is still evident.

In general, this corrosion product layers formed in magnesium exhibit limited protective properties [114] and its composition depends almost entirely on the elements present in solution [41]. However it is important to mention that the major corrosion product Mg(OH)$_2$ from any magnesium alloy is proved to enhance bone growth in vivo [115]. Degradable magnesium alloys adjacent to damaged bone promote osteoblast activity while osteoclast number decrease [115].
5.2. PEO treatment

The initial corrosion rate can be reduced by various mechanical, electrochemical or coating procedures [14]. As a further hypothesis, different magnesium surface properties such as surface roughness, energy and charge could be created by various post-casting treatments.

Plasma electrolytic oxidation was selected as a coating process essentially because these type of coatings are hard when compared with other conversion coatings therefore expected to be more wear resistant [6] and also because as already mentioned (section 2.5) these coatings are usually porous, similar to the cancellous microstructure of bone, which may favour the growth and repair of bone tissue [6] These implant surface properties are reported in the literature to enhance bone bonding to implant surfaces and stimulate adjacent bone growth [126, 127]. The released alloying elements from the coating could be another source to influence bone cell response [14, 128, 129]. Besides, magnesium ions from the corroding magnesium implant and the accompanying local alkalosis could also contribute to the enhanced bone growth [130, 27]

5.2.1. Characterization after PEO treatment

The voltage-time responses for PEO treatments of AZ31 magnesium alloy in silicate and phosphate electrolyte reveal an initial barrier film formation with further development, after visible sparking phenomena occurs at 170 and 190 V, respectively.

In general, for all the solutions and procedures, after reaching a voltage where sparks were visibly less numerous, longer lasting and uniformly distributed across the coating surface, the voltage was kept constant for 25 minutes (procedure fully described in Appendix).

Depending on the electrolyte solution used, some demarked differences can be detached. PEO treatment of AZ31 rods in high concentrated solutions produced coatings with bigger thickness, while low concentrated solutions resulted in lower thickness coatings. The sparking phenomenon was also different; bigger and localized sparks which begin at lower voltages were observed for highly concentrated solutions whereas in the case of low concentrated solutions the starting voltage was higher and small and uniformly distributed sparks were observed. General considerations of the parameters and immediate outcomes are described on table 8. For a proper analysis of the information inserted on the table 8 it is important to clarify the notations used.
PEO treatment was performed only in one electrolyte for tests 1 and 2 – solutions M2 and M3, respectively while for tests 3, 4 and 5, a two-step PEO treatment was performed. The first and the second electrolytes were used independently, but the process was carried for each one as described in Appendix. After treatment in the first solution, the sample was dried, and without any further pre-treatment was anodized in the second bath following the same procedure.

<table>
<thead>
<tr>
<th>Test</th>
<th>Solution</th>
<th>Process</th>
<th>Average thickness (μm)</th>
<th>Maximum voltage (V)</th>
<th>Surface appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M2</td>
<td>DC + pulse</td>
<td>31,5</td>
<td>210</td>
<td>Smooth and homogenous</td>
</tr>
<tr>
<td>2</td>
<td>M3</td>
<td>DC + pulse</td>
<td>2,15</td>
<td>230</td>
<td>Smooth and homogenous</td>
</tr>
<tr>
<td>3</td>
<td>M3</td>
<td>DC + pulse</td>
<td>27</td>
<td>220/220</td>
<td>Slightly coarse</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>DC + pulse</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>M2</td>
<td>DC + pulse</td>
<td>37,5</td>
<td>205/230</td>
<td>Slightly coarse</td>
</tr>
<tr>
<td></td>
<td>M4</td>
<td>DC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>M4</td>
<td>DC + pulse</td>
<td>35</td>
<td>250/220</td>
<td>Slightly coarse</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>DC + pulse</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The addition of polyamine on low concentrated solution M4 resulted in a rise of the starting and maximum sparking voltage to 195V and 250V, respectively.

The use of pulse current programme originated more uniform sparks reducing therefore the defect risk.

EIS evolution in SBF for the samples anodised under the conditions described on table 8 are disclosed on figures 28 and 29.
Figure 28 Bode plots of AZ31 treated samples in different electrolytes (M2, M3, M3 + M2, M2 + M6 and M6 + M2) after immersed in SBF for 5, 10 h and 1 day (EIS measurements by dr. Anna Zych).
Figure 29 Bode plots of AZ31 treated samples in different electrolytes (M2, M3, M3 + M2, M2 + M6 and M6 + M2) after immersed in SBF for 2 days (EIS measurements by dr. Anna Zych).

Figure 30 Bode plots of AZ31 treated samples in M3 electrolyte after immersed for 5, 10h, 1, 2 and 3 days. The impedance values were kept constant. (EIS measurements by dr. Anna Zych).
In the early stages of immersion in SBF, electrochemical tests (EIS) revealed reduced corrosion current densities by more than two orders of magnitude. However, for longer immersion times in the case of silicate/fluoride (M2) electrolyte, the PEO coating failed due to probable formation of a corrosion layer beneath the coating. Although it produces a thinner coating, phosphate containing solution (M3) revealed a much improved corrosion behaviour with no signs of pitting corrosion in the coating. In fact, as observed on Figure 30, the corrosion performance in SBF increases slightly and after 1 day is kept constant till the end of the third day.

When PEO treatment was performed in both electrolytes, in the second step of the process there is a competition between old film dissolution and new film formation [72]. Good results were obtained when phosphate containing electrolyte was used in the first step since a more compact layer was formed between the substrate. These two different layers can be observed on cross section figures 32, 33 and 34 (b). Phosphate anions are known to enhance the growth rate and the compactness of the oxide coating. Besides, phosphate has a sealing effect in the coating build-up resulting in a more protective coating as inferred on EIS spectra. [70].

The following SEM analysis was performed by Dr. Alicja Bałkowiec from the Materials Engineering Group, Warsaw.

![Figure 31 SEM images of AZ31 after PEO treatment in M2 solution](image1)

**Figure 31** SEM images of AZ31 after PEO treatment in M2 solution

![Figure 32 Chemical content along cross section of AZ31 after PEO treatment in M2 solution.](image2)

**Figure 32** Chemical content along cross section of AZ31 after PEO treatment in M2 solution.
Figure 33 SEM images of AZ31 after PEO treatment in M3 solution.

Figure 34 Chemical content along cross section of AZ31 after PEO treatment in M3 solution

Figure 35 SEM images of AZ31 after 2-step PEO treatment in M3 and M2 solution.

Figure 36 Chemical content along cross section of AZ31 after 2-step PEO treatment in M3 + M2 solution.
Figure 37 Chemical content along cross section of AZ31 after 2-step PEO treatment in M4 + M2 solution.

Figure 38 Chemical content along cross section of AZ31 after 2-step PEO treatment in M2 + M4 solution.

Figure 39 SEM images of AZ31 after 2-step PEO treatment in M4 and M2 solution.

Figure 40 SEM images of AZ31 after 2-step PEO treatment in M2 and M4 solution.
PEO treatment of AZ31 magnesium alloy in silicate electrolyte for 2400 s produced coatings of approximately 31 μm whereas in phosphate electrolyte, the same process and time produced coatings with no more than 3 μm. Both treatments resulted in coatings with relatively smooth surfaces revealing pores and cracks typical of the process however, for phosphate electrolyte the coating is more homogenous and compact. Cross-sections showed an outer relatively dense layer and large cavities in the inner region of the coating. When both electrolytes were applied during the PEO treatment two different zones were easily distinguished in the cross-section images. EDS analysis also revealed (see Figures 32, 34, 36, 38 and 40) that the main constituents include MgO and MgSi and Mg₃(PO₄)₂ when immersed in M2 or M3 and M6 respectively, indicating the presence of species derived from both the substrate and the electrolyte.

Formation of P-containing oxide films create a substrate for faster precipitation of calcium phosphates from SBF solutions. Plugging of the pores by this deposit inhibits further degradation of the oxide film.

It is worth to refer that, once anodized surfaces are generally porous, anodized magnesium alloys are usually intended to be later sealed or covered by protective layers, in order to effectively protect magnesium alloys from corrosion in aggressive environments for a long period of time. In the case of unsealed coatings, it has been found that the corrosion resistance provided by the same anodic coating depends significantly on the composition of the magnesium alloy, and overall, the corrosion resistance of the coating was closely associated with the corrosion performance of the substrate alloy [70, 120, 132].

Song [123], has suggested that a potential magnesium-based implant should possess six times lower hydrogen evolution rate than AZ91 alloy. When comparing the present electrochemical experimental results of PEO treated AZ31 samples (M3, M3 + M2) with the bare AZ31 samples, the improvement in the corrosion resistance achieved is very encouraging. The EIS results are almost two orders of magnitude higher for the PEO coated samples, when compared with blank AZ31 samples.
6. Conclusions and Future Work

This work reviews the biological performance of two different magnesium based alloys (biodegradable materials for temporary implant), WE54 and AZ31 alloys in 0.05 M NaCl and Hank’s solution at room temperature and 37°C. Their corrosion behaviour was studied by the analysis of corrosion resistance variation with immersion time using electrochemical impedance spectroscopy tests and confirmed using scanning electron micrography and x-ray photoelectron spectroscopy. The aim is to explore possible routes to improve limiting factors such as the corrosion resistance highlighting the need for further research to take advantage of Mg corrosion mechanisms to obtain tailored biodegradable metallic implants.

The EIS data are only treated qualitatively since it is first necessary to assess the corrosion processes behind the complex degradation progression with and without temporary surface protection (PEO treated).

The main aspects worth to emphasize are summarized as follows:

- The electrochemical tests demonstrated that, in general, WE54 revealed a better impedance response although it presented a lower open circuit potential for all the solutions and conditions tested.

- In NaCl, AZ31 and WE54 revealed identical impedance response and their corrosion products presented a typical brucite-like structure.

- In Hank’s solution, at room temperature both alloys showed an improved corrosion resistance, with the impedance values increasing with time of immersion. In contrast, at 37°C the corrosion resistance decreased, especially for WE54 which presented an impedance response lower than AZ31.

- EIS is sensitive to the formation of different types of degradation products formed on the surface. In Hank’s solution an extra time constant was observed for both alloys. This is caused by the formation of adherent corrosion products on the sample surface such as Mg(OH)₂ and calcium phosphate products (particularly hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂) which are responsible for an increase in the protectiveness of the sample. These products precipitate from the solution during the corrosion of magnesium alloys due to saturation and localized alkalization.
Accumulation of corrosion products was faster in AZ31 with a thicker but inhomogeneous layer forming, particularly in Hank’s solution where, besides Mg(OH)$_2$, deposition of phosphates, chlorides and calcium was observed.

Although they do not significantly increase the corrosion resistance of the alloys, these corrosion products improve largely the biocompatibility and osteointegration of the magnesium implant.

A second aspect related to biodegradable implants is clearly to avoid corrosion in a first period in order to guarantee the mechanical integrity and the functionality of the implants. This is difficult to achieve with a bare alloy surface therefore plasma electrolytic oxidation has been used to grow protective coatings in AZ31 alloy using different electrolytes and DC and pulse current processes.

PEO treatment led to a substantial improvement of the corrosion resistance especially on phosphate electrolyte due to the penetration of solution into the alloy substrate probably inducing the formation of a uniform magnesium hydroxide layer beneath the coating.

The corrosion protection of AZ31 achieved with PEO treatment does not correlate necessarily with the relative corrosion resistances in the untreated conditions, but essentially depends on the coating properties since it is primarily influenced by the alloy composition.

The promising future of Mg and its alloys is dependent on being able to control the rate of corrosion in body fluids. The encouraging results obtained in this work after the PEO treatment represent the basis for future research.

Self-ordered nanotubular and nanoporous coatings obtained after PEO treatments [133 - 136] are reported to improve the corrosion rate of the magnesium substrate, which, allied with the further sealing with a hydroxyapatite silane, could improve largely not only the degradation rate but also the biocompatibility of the implant, the two main aspects that have to be addressed.

Recently, calcium addition to magnesium alloys was reported to improve the general corrosion resistance in chloride containing environment due to the refinement of the microstructure [111, 122]. Calcium is biocompatible and a major constituent of bone. Therefore, this could also be considered for the next approach and the corrosion behaviour of PEO treated calcium enriched alloys analysed.
Finally, localized electrochemical impedance spectroscopy (LEIS) measurements to characterize the corrosion performance and the defects formation in the magnesium sample in real-time and at the microscopic level should also be considered in the next steps.
7. References


46. NACE Basic Corrosion Course, National Association of Corrosion Engineers, Houston 1971


48. M. G. S. Ferreira, Corrosão e Protecção, Instituto Superior Técnico, 2001


Appendix

General Plasma Electrolytic Oxidation Procedure

1st Test – Program 1
\( U_1 = 1V; U_2 = 1V; T_1 = 10s; C = 30 \text{ cycles} \)
(final voltage: 30V);

2nd Test – Program 1
\( U_1 = 30V; U_2 = 2V; T_1 = 20s; C = 20 \text{ cycles} \)
(final voltage: 70V);

3rd Test – Program 1
\( U_1 = 70V; U_2 = 2V; T_1 = 20s; C = 20 \text{ cycles} \)
(final voltage: 110V);

4th Test – Program 1
\( U_1 = 100V; U_2 = 2V; T_1 = 20s; C = 30 \text{ cycles} \)
(final voltage: 160V);

5th Test – Program 1
\( U_1 = 140V; U_2 = 2V; T_1 = 20s; C = 30 \text{ cycles} \)
(final voltage: 200V);

According to the electrolyte sparkles will start between 170 – 200 V
6<sup>th</sup> Test
Program 1 - \(U_1 = 180V; \ U_2 = 2V; \ T_1 = 20s; \ C = 10 \) cycles
(final voltage: 200V)
Program 2 – \(U_1 = 200V; \ T_c = 1500s;\)

Fig. A2. – Program 2 – Constant potential

7<sup>th</sup> Test
Program 1 - \(U_1 = 180V; \ U_2 = 2V; \ T_1 = 20s; \ C = 10 \) cycles
(final voltage: 200V)
Program 3 – \(U_1 = 205V; \ U_2 = 0V; \ T_1 = 10 \) ms; \(T_2 = 10 \) ms; \(T_c = 1500s;\)

Fig. A3. – Program 3 – Pulse current